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DEVELOPMENT OF IMPROVED PYROELECTRIC DETECTORS

Literature survey of pyroelectric materials and their characteristics

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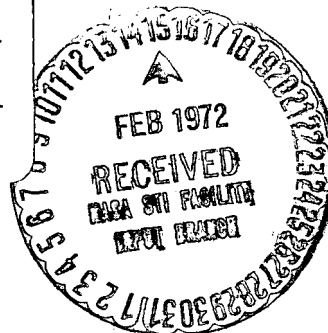
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16. Abstract <p>The object of this program is to improve the detectivity of the pyroelectric detector with the ultimate goal of operation at or near the temperature-noise limit. Two general areas of investigation are undertaken. The first is to improve responsivity through the use of new materials. The second is directed toward reduction of noise and will be effected with improved field effect transistor characteristics, and improved electroding of the pyroelectric material.</p> <p>The search for new materials has begun with a review of the literature on pyroelectric materials in several languages. The compiled data includes an extensive list of references. From this, several materials have already been selected for investigation.</p> <p>FET's are being obtained from various manufacturers, evaluated, and selected units will be tested with pyroelectric elements as complete detectors.</p>			
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PREFACE

The object of this program is to improve the detectivity of the pyroelectric detector with the ultimate goal of operation at or near the temperature-noise limit. Two general areas of investigation are undertaken. The first is to improve responsivity through the use of new materials, the use of thinner sections of material, and through the application of the dielectric mode. The second is toward reduction of noise through improved field effect transistor characteristics and improved electroding of the pyroelectric material.

The search for new materials has begun with a review of the literature on pyroelectric materials. This will continue for the duration of the program. The literature search will result in a compilation of potentially useful materials and their available characteristics. An extensive list of references is included.

As the data is collected, it is reviewed and materials are selected for investigation. Materials will be purchased if available. Crystals that are not available but can be grown from saturated aqueous solutions, will be grown at Barnes Engineering. Materials of interest will be examined and their pertinent characteristics measured. The more promising materials will be processed into detectors so that the detector characteristics may be measured and evaluated. Part of the detector construction effort will be devoted to the development of techniques for obtaining thin sections of pyroelectric material, and for the investigation of electroding techniques.

Field Effect Transistors (FET's) will be obtained from various manufacturers and evaluated for those characteristics affecting detector performance. FET's exhibiting improved characteristics will be tested with pyroelectric elements as complete detectors.

During the period of this report, the bulk of the literature search was completed and several materials selected for further study. Some specialized

test equipment has been designed and construction started.

Project accomplishments to date are consistent with the objectives of the program.

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Section 1.0 INTRODUCTION

The first phase of this program has been carried out over a three month period beginning August 20, 1971 and ending November 22, 1971.

The goals for this phase are listed:

1. Complete the major portion of the literature search. The literature search will be continued for the duration of the program.
2. Complete the major portion of a compilation of all materials potentially suitable for detectors and their available characteristics as derived from the literature search.
3. Purchase or begin the crystal growing of those materials that are immediately recognized as being of interest.
4. Define the measurements and test equipment required for the program. Design special equipment, purchase components, and begin construction.
5. Begin measurement of characteristics as material and equipment becomes available.

These goals were achieved, and each is discussed in turn in the remainder of this report.

Section 2.0 LITERATURE SEARCH

The available literature was culled for materials potentially useful in the infrared. The selection of papers was limited to those written in or translated into English, French, or German that discuss materials or techniques suitable for application in infrared pyroelectric detectors. Useful operating temperatures were limited to the approximate range of 195°K to 400°K. The literature search resulted in a compilation of potentially useful materials and their available characteristics. For each material, the following data was collected:

1. Pyroelectric Coefficient.
2. Curie Temperature.
3. Dielectric Constant and measurement frequency.
4. Loss Tangent and measurement frequency.
5. Thermal Capacitance.
6. A-C Resistivity (derived from loss tangent).
7. Figures of Merit (Sensitivity and Detectivity).

The compilation of materials and characteristics has resulted in the table in Appendix A of this report. The extensive list of references is noteworthy. The table will be expanded as additional information is obtained from current literature.

Section 3.0 SELECTION OF MATERIALS FOR INVESTIGATION

On the basis of all available data (see Appendix A) regarding the respective Figures of Merit for Responsivity and Detectivity the following materials (in two groups) have been selected for complete testing:

Group 1 (materials on hand or on order):

TGS

DTGS

TGFB

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

TGS/Se (15% Se)

$\text{TGS}_{0.88}\text{TGFB}_{0.12}$

$\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$

LiTaO_3

Polyvinylidene Fluoride

Group 2 (materials still to be grown or irradiated):

TGS with subsequent X-, γ -, and UV-irradiation

TGS/Se ($\sim 15\%$ Se plus additives, possible Cu^{+2} or Cr^{+3})

TGS/Se ($\sim 5\%$ Se)

DTGSe

NaNO_2

3.1 REASON FOR MATERIAL CHOICE

TGS - most available data to date.

DTGS and TGFB - higher Curie temperature than TGS, permitting higher ambient temperatures.

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ - has rather flat responsivity over a wide temperature range; also, can withstand higher relative humidity than TGS.

TGS/Se (either 5% or 15% Se, with or without additional doping) - these currently are reported to give the best detector performance.

TGS-TGFB - Since TGS and TGFB are completely miscible in all proportions, a crystal was grown from an equimolar solution of TGS and

TGFB. In agreement with Brezina et al. (B6) a crystal with $\text{TGS}_{0.88}\text{-TGFB}_{0.12}$ ratio was obtained. Since this crystal is available and has a higher Curie temperature than TGS, it was also included.

SBN - This material has been cited repeatedly in the recent literature as a promising pyroelectric detector material. A barium content of 25% appears as the optimum composition.

LiTaO₃ - The very high Curie temperature permits this material to be used at very high ambient temperatures or energy levels.

Polyvinylidene Fluoride - Even though the expected detectivity of this material is an order of magnitude lower than TGS, it is included for further examination since it permits very economical construction of large area detectors or arrays.

TGS with X-ray, Gamma ray, or U-V-Irradiation of biased TGS causes locked-in polarization which inhibits depoling.

DTGSe - Ordinary TGSe would be an excellent pyroelectric detector material if it were not for its low Curie temperature (22.2°C). Deuteration raises the Curie temperature to a possible acceptable level (34.5°C).

NaNO₂ - was included because of its high Curie temperature and apparently low loss tangent.

3.2 REASON FOR MATERIAL OMISSION

Colemanite - has been omitted even though its parameters look extremely promising because the naturally occurring material has varying impurities (depending upon its source) which do not permit duplication of results. Moreover, it is difficult to obtain good crystal samples.* The synthetic Colemanite can only be grown as microcrystals which appear unsuitable for the current investigation.

GUL - has been omitted temporarily until more information regarding its growth or source of procurement becomes available.

*according to Dr. H. H. Wider of Naval Electronics Lab., San Diego, Calif.

Section 4.0 MEASUREMENTS

Measurements have been divided into three general categories. These are: measurement of material characteristics, measurement of FET characteristics, and measurement of detector characteristics.

4.1 MATERIAL CHARACTERISTICS

The literature search has disclosed wide variations in some of the material characteristics as reported by different investigators. The test conditions are sometimes unknown. At times the reported test conditions vary widely from the detector test conditions, which makes the usefulness of the material characteristics questionable.

All materials of interest that can be obtained by growth or through purchase will be tested to determine their characteristics on a wider and more thorough basis than has been previously reported. The measurements to be made are listed and the techniques and associated equipment are discussed below. Section 4.1.4 describes the material preparation prior to these tests.

4.1.1 Dielectric Constant and Loss Tangent

These will be measured as functions of frequency, bias (unless permanently polarized), and temperature. Frequencies will range from 20 Hz to 10 KHz. The specific frequencies are 20, 100, 1K and 10KHz. Temperatures will range from approximately -30°C to 5°C higher than the Curie temperature with a maximum temperature of 100°C . Bias voltages will be 0.01, 1, 10 and 50 volts. Capacitance and loss tangent will be measured on a General Radio Bridge, Type 1620 equipped with a variable bias supply. The dielectric constant will be derived from the capacitance and the pyroelectric specimen dimensions. A thermoelectrically cooled or heated sink will be used to set the temperature of the specimen.

4.1.2 Pyroelectric Coefficient

The pyroelectric coefficient will be measured by recording the change of electrical charge exhibited by a pyroelectric specimen with the corresponding change in temperature, using an X-Y recorder. The slope of the

recorded curve indicates the pyroelectric coefficient at the corresponding temperature. The same thermoelectric cooler-heater mentioned in 4.1.1 will be used to set the specimen temperature.

The electrical circuits used in the measurement of pyroelectric coefficient are shown in Figures 4-1 and 4-2. Temperature is displayed on the X-axis of the recorder. An iron-constantan thermocouple with an electrical reference junction is connected to a chopper-stabilized amplifier. The output is further amplified, inverted, and then applied to the recorder.

The charge produced by the pyroelectric material as it is subjected to a temperature change is recorded on the Y-axis of the recorder. The electrodes of the sample are connected to a charge-integrating amplifier located close to the sample holder. The signal passes through a second amplifier and then to the recorder. Since the integrating amplifier cannot integrate indefinitely, a shorting switch has been provided to discharge the amplifier. This will be done manually at approximately 3 to 4 minute intervals. At a later date, an automatic discharge system will be considered. The measured charge accumulated during a given temperature interval provides information for the calculation of the pyroelectric coefficient.

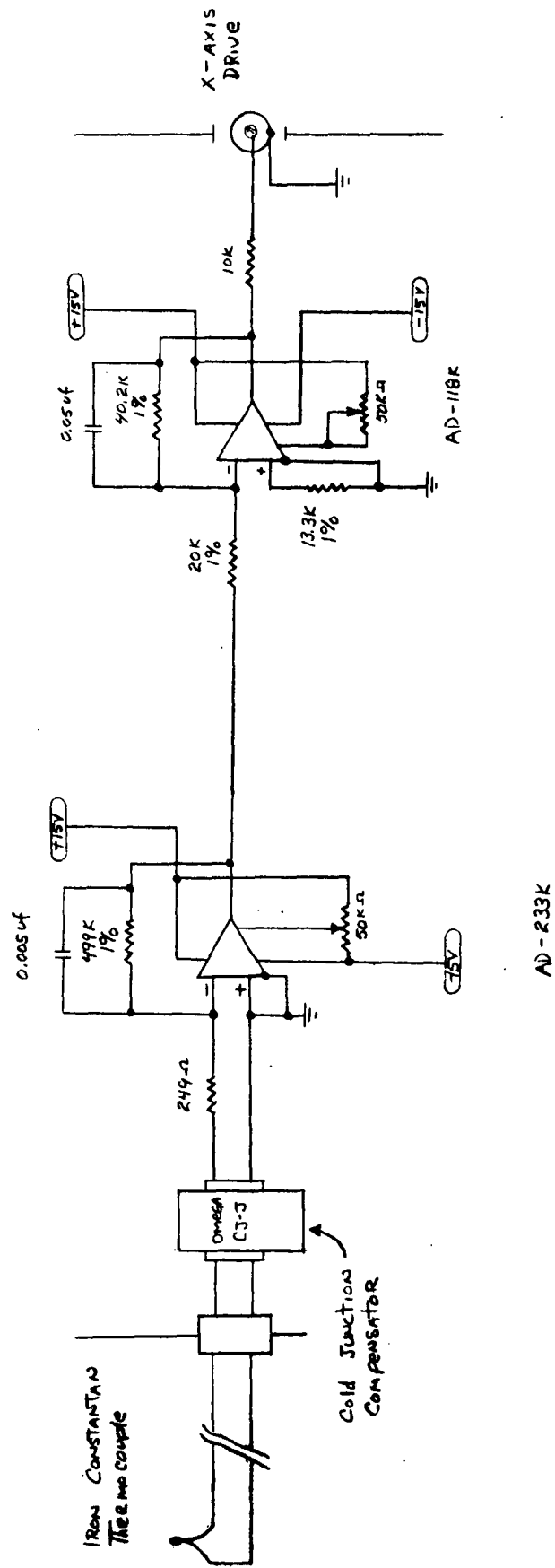
4.1.3 Transmittance and Reflectance

The Beckman DK-2 Spectrophotometer is used to measure transmittance and total reflectance from 0.3 to 3μ . Specular reflectance and transmittance in the range of 2 to 40μ is measured with a Beckman IR-20 Spectrophotometer. Measurements are made with no electrodes and again with a transparent nichrome electrode on one side of the sample.

The data obtained from these measurements is reported in Appendix B.

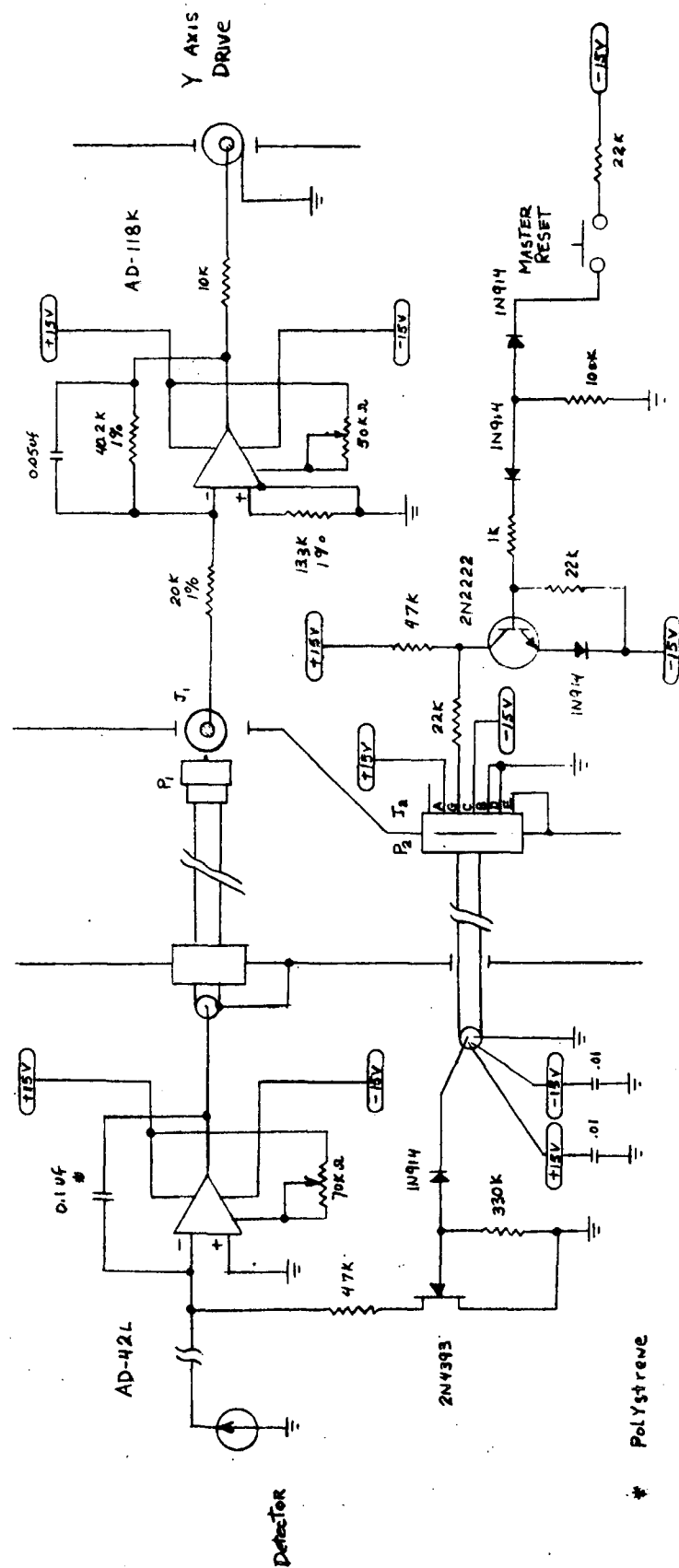
4.1.4 Sample Preparation

Material for the various measurements is prepared as shown in Table 4-1. The samples are mounted and housed in a container consisting of a four-pin metal header and a copper cover, Figure 4-3. The pyroelectric material sample is mounted directly to the metal header so that its temperature may be controlled and measured. Wire leads from the sample connect to the



4-1 THERMOCOUPLE AMPLIFIER CIRCUIT FOR PYROELECTRIC COEFFICIENT MEASUREMENT

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4-2 CHARGE AMPLIFIER CIRCUIT FOR PYROELECTRIC COEFFICIENT MEASUREMENT

feed-through pins. The cover is cemented to the header with epoxy resin. No window is required for the dielectric constant, loss tangent, and pyroelectric coefficient measurements. The mounting for the responsivity measurements contains a KRS-5 window.

After the sample is mounted in the holder, the holder is attached to the thermal sink and coupled to the preamplifier as shown in Figure 4-4. All samples thus share the same environment and the same electrical signal processing.

4.2 FET Characteristics

There is some evidence that pyroelectric detector sensitivity is limited principally by noise associated with the FET impedance converters. Measurements will be made to select the best possible FET's for use in this application. The following characteristics are to be measured on a reasonable sampling of candidate FET's purchased for the program:

1. Gate Leakage Current
2. Current Noise vs. Frequency and Temperature
3. Short Circuit Noise
4. Transconductance
5. Input Capacitance

4.2.1 Leakage Current

To achieve low noise in a pyroelectric detector system a principal requirement is to start with an FET that has low gate leakage current (I_{GSS}) and hence low current noise. At the same time this permits use of a large-value load resistor which, at high frequencies, leads to low Johnson noise. Direct measurement of low leakage currents of the order of 1 pA is complicated when one is dealing with components operated in an open (humid) environment. A small chamber has been made up to free the input components (FET and gate load resistor) from humidity effects by vacuum pumping. The output characteristics can then be measured to indicate the leakage current.

TABLE 4-1 MATERIALS PREPARATIONS FOR CHARACTERISTIC MEASUREMENTS

Process	1	2	2A	3	4
Measurement	Transmittance, Reflectance 0.3 to 40 μ	Transmittance, 0.3 to 40 μ	Transmittance, 0.3 to 40 μ	Dielectric Constant, Loss Tangent, Pyroelectric Coefficient	Responsivity, Noise
Material Preparation	Cleave, slice and lap to approx. 1 mm thick	Lap half the material in column 1 to approx. 0.1 mm thick	From Column 2	Cut 5 x 5 mm section from remaining material in column 1	Lap remaining material in column 2A to 0.04 mm. Preserve transparent coating.
Size	As lapped	As lapped	As lapped	5 x 5 x 1 mm	1.5 x 1.5 x 0.04 mm
Coating	None	None	One side Transparent Nichrome - 300 ohms per sq.	Side 1 - transparent Nichrome Side 2 - Opaque Nichrome	Side 1 - transparent Nichrome Side 2 - Opaque Nichrome
Mounting	None	None	None	4 pin base and copper cover	4 pin base, copper cover with KRS-5 window

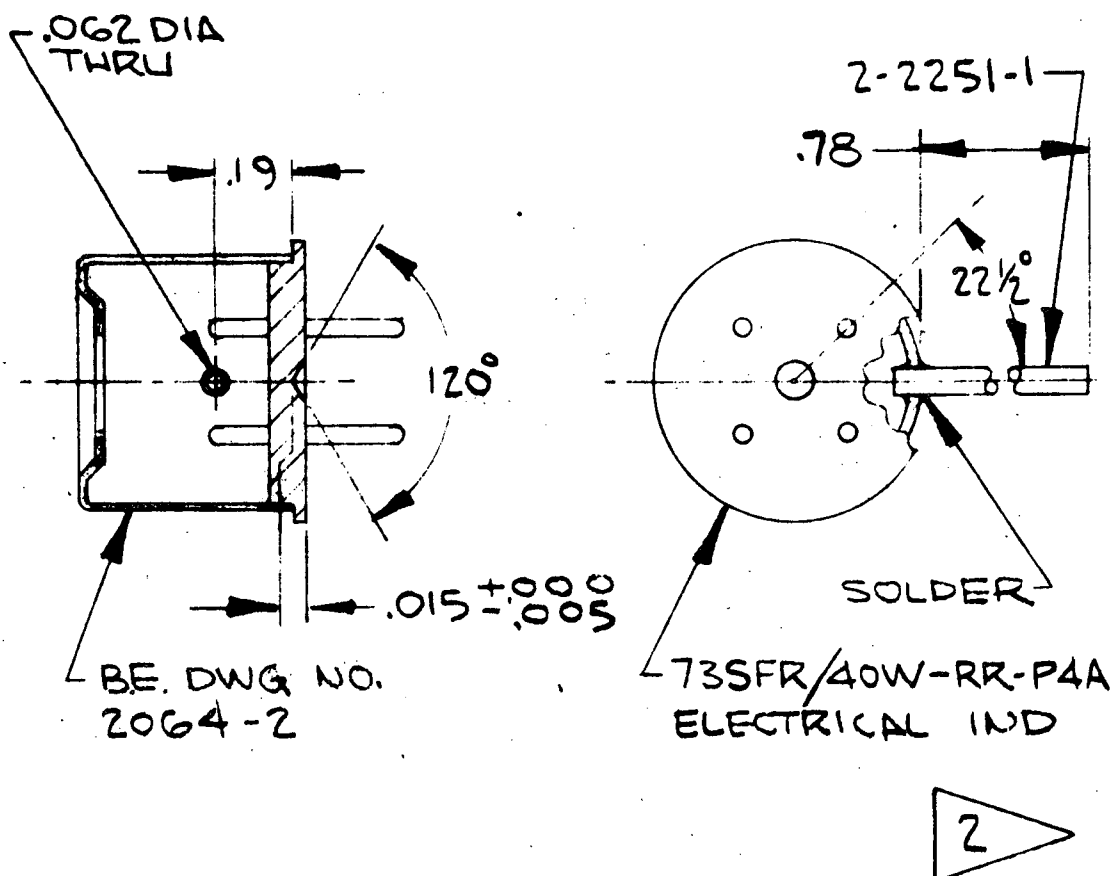


Figure 4-3 PYROELECTRIC SAMPLE HOLDER CONSTRUCTION DETAIL

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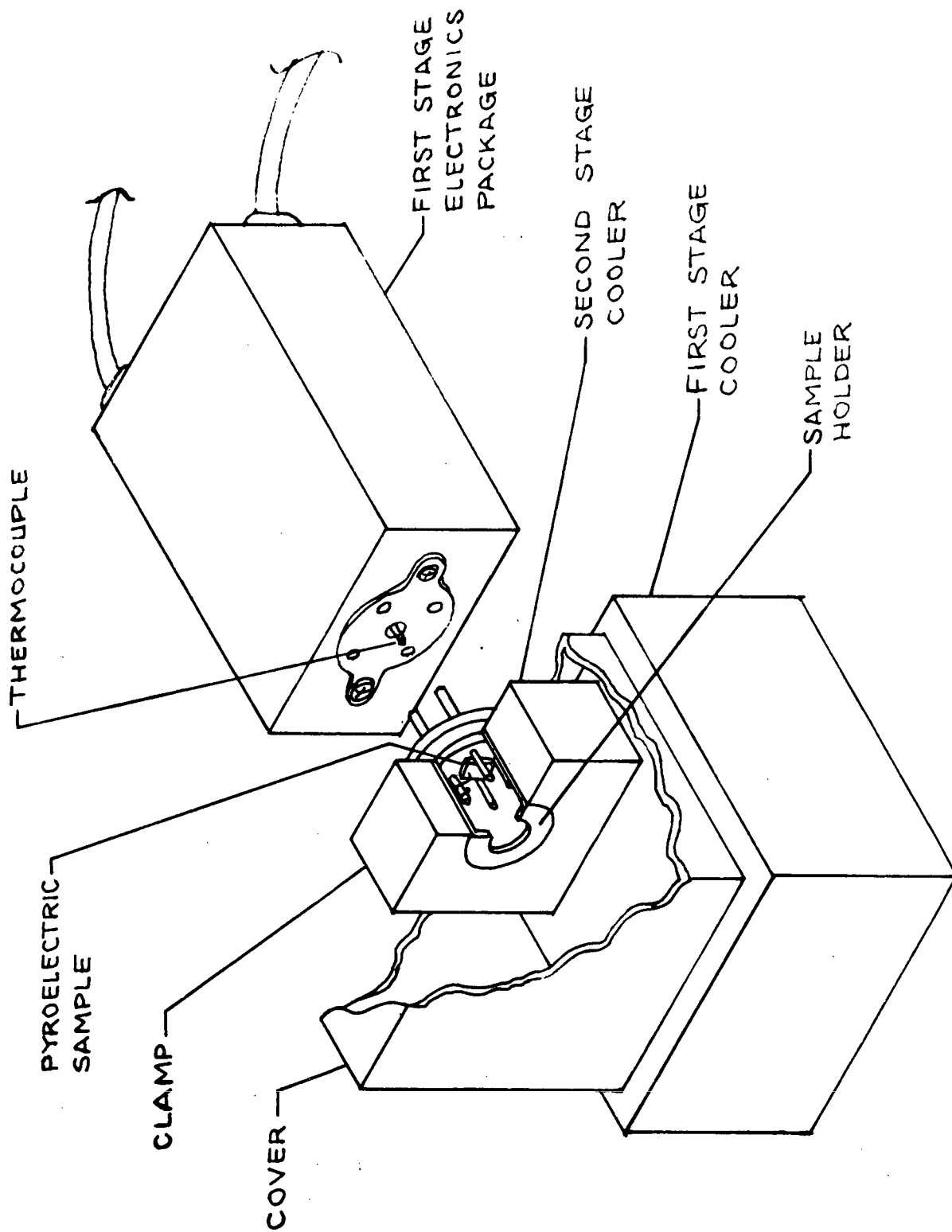


Figure 4-4 SAMPLE TEST SETUP

4.2.2 Leakage Current Noise

Leakage current induced noise is difficult to identify as such in the conventional mode of operation. The contribution to the measured output noise by the Johnson noise of the gate input resistor (R_L) and the possible detector loss resistance may be indistinguishable from noise due to the gate current. This condition can be modified by making measurements using several values of load resistance and replacing the detector element with known, low loss resistance capacitors. Figure 4-5 shows some typical noise curves. When using high values of load resistance (e.g. $R_L = 10^{12}$) the system is expected to be current-noise limited at all frequencies. For relatively low values of load resistance ($R_L < 10^{10}$) it may be Johnson noise limited (the noise being attributable to R_L). The readings obtained should permit positive identification and measurements of the noise constituents, both current and Johnson noise sources. These measurements are first made at room temperature. It is important that the amplifier following the FET be a low-noise device that will not degrade the measured response.

The measurements are also repeated at temperatures other than 20°C. These measurements will also provide clues to the character of the noise. A temperature increase by 20°C should increase the leakage current by 4 times and is expected to double the current noise.

4.2.3 Short-Circuit Noise

Noise measurements at high frequencies will indicate the short circuit noise of the FET's tested.

To extend the short circuit noise measurement to lower frequencies we plan to bypass the FET gate input resistor with a large value capacitor, and make noise measurements with a wave analyzer over a wide range of frequencies.

4.2.4 Transconductance

To be useful the FET's to be tested must have a minimal G_m of 500. Whether used in a common source or common drain configuration, the FET must provide gain in terms of voltage amplification or impedance conversion.

$$\text{Johnson Noise, } V_{nJ} = \left[\frac{4KT R_L}{1 + \omega^2 \tau_e^2} \right]^{1/2}$$

$$\text{Shot Noise, } V_{nSh} = \left[\frac{2qI_{GSS} R_L^2}{1 + \omega^2 \tau_e^2} \right]^{1/2}$$

$$\text{Assume: } I_{GSS} = 1 \text{ pA}$$

$$C_D = 4 \text{ pf}$$

$$\therefore I_{Sh} = \sqrt{2qI_o \Delta f} = 6 \times 10^{-16} \text{ A Hz}^{-1/2}$$

$$\tau_e = R_L C_D$$

$$f_e = \frac{1}{2\pi\tau_e} = \frac{1}{2\pi R_L C_D}$$

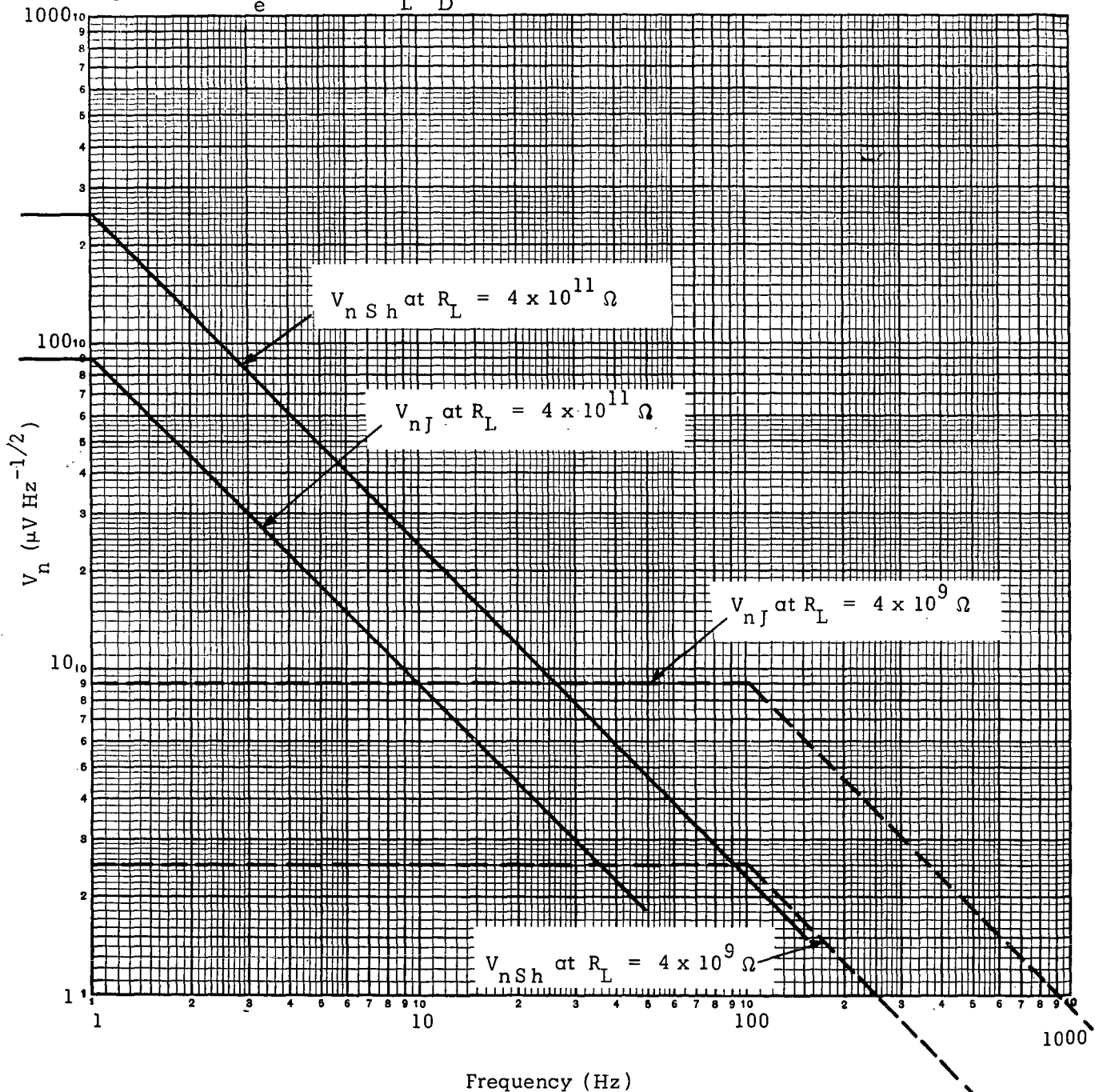


Figure 4-5 FET NOISE CHARACTERISTICS

In the common drain configuration normally used in this application, the transconductance can be determined simply from a measurement of the output impedance of the FET (in this case, source follower output impedance). This is done by feeding a small signal into the gate and measuring the source follower output voltage with varying load impedances applied until the output voltage drops to a measurably attenuated value (e.g. 1/2).

4.2.5 Input Capacitance

The detector input capacitance, which is essentially a shunt impedance to the detector capacitance and represents a loss in signal transferred into the amplifier, can be readily measured by determining the frequency response or high frequency cut-off point when feeding signals into the gate through a fixed and known source resistance.

If we apply to the FET gate a signal from an oscillator in series with a resistor (R_s) of $10^7 \Omega$, and the FET output drops by 3 DB at a cutoff frequency (f_{hf}) 10 KHz, then the FET gate input capacitance, C_{iss} , is 1.6 pf, i.e.

$$C_{iss} = \frac{1}{2\pi R_s f_{hf}}$$

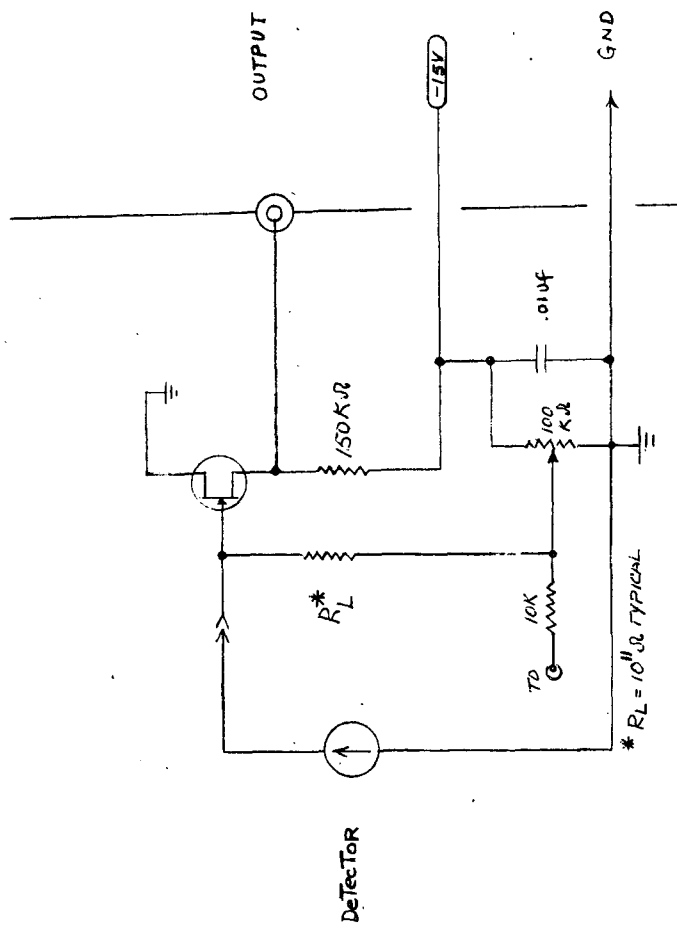
The test equipment for the tests discussed above is at hand. Three samples each of three types of FET have been obtained. Orders are now being placed for several others which have characteristics that appear to be promising. Measurements will be started in the next several weeks.

4.3 MEASUREMENT OF DETECTOR CHARACTERISTICS

Materials are measured for responsivity and noise using the same thermoelectrically heated or cooled sink as in 4.1.1. The electronics for this test are shown schematically in Figures 4-6 and 4-7. The electronics are located outside of the pyroelectric sample container. This permits the same electronics to be used with all samples. The FET source follower is located close to the sample holder and its output is coupled by cable to the input of a low noise amplifier. The output of the amplifier will be read on a Hewlett-Packard Wave Analyzer in RMS volts. A blackbody and variable

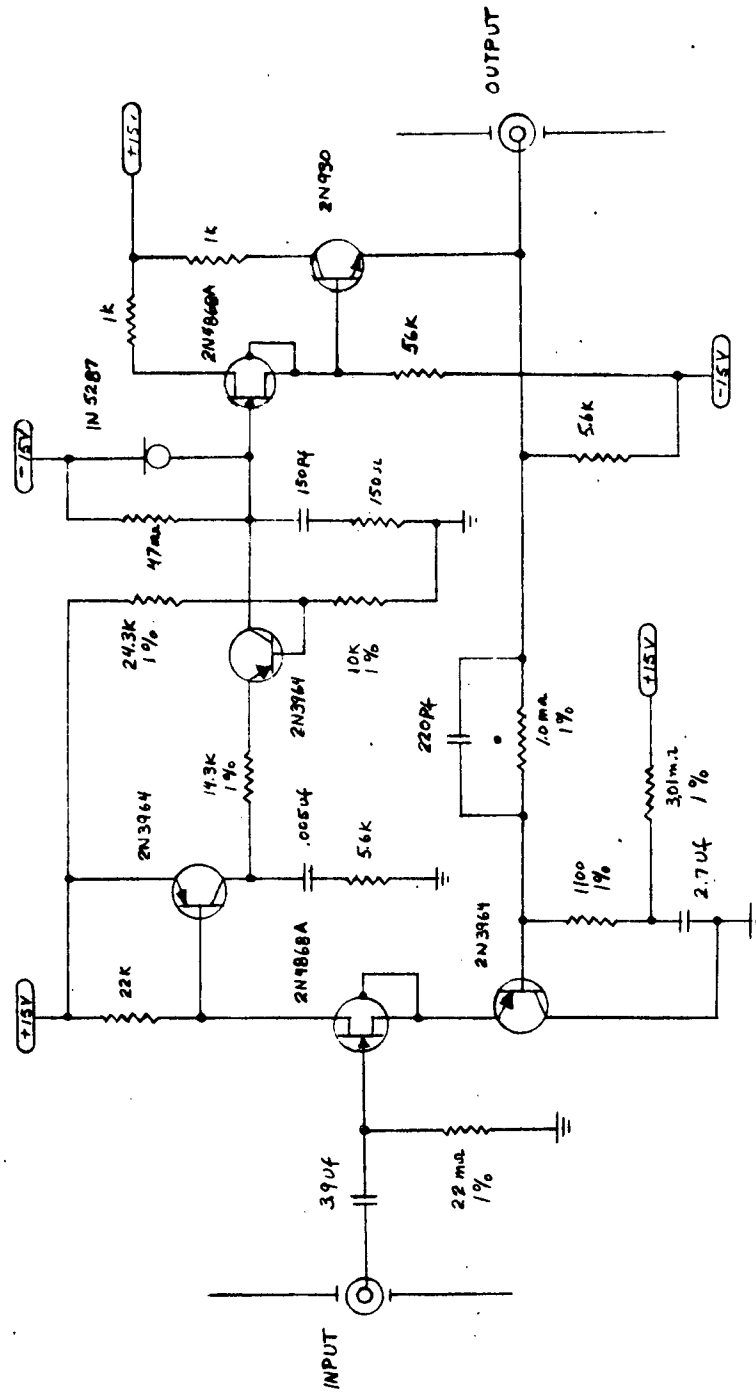
speed chopper are used to irradiate the sample.

The same system is used to measure noise except that no radiant energy is required. Noise is measured in a 7 Hz bandwidth and is calculated for a 1 Hz bandwidth.



* $R_L = 10^{11}\Omega$ TYPICAL

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4-6 SOURCE-FOLLOWER CIRCUIT FOR DETECTOR RESPONSIVITY AND NOISE MEASUREMENT



A23427

4-7 PREAMPLIFIER CIRCUIT FOR RESPONSIVITY AND NOISE MEASUREMENT

Section 5.0 NEW TECHNOLOGY

During this report period there were no technical developments reportable under the New Technology Clause of the subject contract.

Section 6.0 PLANNED FOR THE NEXT REPORTING PERIOD

The search for more pyroelectric materials (whose parameters might lead to satisfactory I-R detector operation) will continue, and the table of material parameters will be continuously updated with the most valid data.

Transmittance and reflectance measurements will continue on 1 mm as well as 0.1 mm thick samples.

On completion of the test equipment, the dielectric constant and loss tangent as functions of frequency and temperature will be determined for all available materials. The anticipated measurements will range in temperature from -30°C to 100°C at respectively 20, 100, 1K, and 10K Hz. The effect of bias on the dielectric constant and loss tangent will be investigated. The pyroelectric coefficient will also be measured over the indicated temperature range. If time permits during the next reporting period, detector elements $1.5\text{mm} \times 1.5\text{ mm} \times 0.04\text{mm}$ will be processed from the most promising detector materials. Subsequently, responsivity, noise, detectivity, and spectral response measurements will be made on these evacuated flakes as functions of temperature and frequency. The search for improved transistors and detector operation will continue simultaneously.

The effect of gamma and U-V-irradiation on TGS and DTGS will be investigated as well as the effects of Cu^{++} and Cr^{+++} doping. Either of these techniques should lead to "locked-in" polarization of single domains. This causes a shift in the hysteresis curve and implies that a detector will not have to be repoled after exceeding the FET temperature.

Measurements of sample FET's will begin.

Section 7.0 CONCLUSIONS AND RECOMMENDATIONS

The project accomplishments during the reporting period are consistant with the objectives of the program. Material procurement and testing are still in process, and the results are incomplete. There is no basis for altering goals.

APPENDIX A - COMPILATION OF PYROELECTRIC MATERIALS AND THEIR CHARACTERISTICS.

TABLE A-1. PYROELECTRIC MATERIALS CHARACTERISTICS

MATERIAL	Curie Temperature T_c °C	Temperature of Measurement T °C	Dielectric Constant ϵ	Frequency of Measurement f Hz	Spontaneous Polarization P_s $C\text{ cm}^{-2} \times 10^{-6}$	Pyroelectric Constant dP_s/dT $C\text{ cm}^{-2} \cdot ^\circ K^{-1} \times 10^{-8}$	Specific Heat c $J\text{ cm}^{-3} \cdot ^\circ K^{-1}$	Density ρ $g\text{ cm}^{-3}$	A.C. Resistivity (1 KHz) ρ $\Omega\text{-cm}$	$(dP_s/dT) \epsilon^{-1}$ $\times 10^{-10}$	$(dP_s/dT) (\epsilon \cdot c)^{-1}$ $\times 10^{-10}$	$(dP_s/dT) \rho^{1/2} \epsilon^{-1}$ $\times 10^{-4}$	Reference	COMMENTS
LiNbO ₃	1200 ± 10	27	30	1K, 100K	50	0.4	2.8	4.65	9.8×10^{10}	1.3	0.46	4.5	N1, P1, S1	T_c depends on crystal composition; varies from 1150°-1245° C. Transmits 0.4-5.0 μ
		100	30	100 K	49.5	0.5				1.7	0.61			
		200	30	100 K	49	0.7				2.3	0.82			
		450	40	100 K	46									
LiTaO ₃	660,	25	47	1 K	50	1.9	3.16	7.45	$\sim 1 \times 10^{10}$	4.0	1.3	6	G1, G2	T_c depends on crystal composition, varies from 660°-560° C.
	618 for	250	70	10 K	45	2.1	3.72			3.0	0.81		M1, Y1	Transmits 0.5 to 5 μ (3 μ absorption).
	$T_a/Li = 1.1$	450	300	10 K	37.7	8.2	3.84			2.7	0.71		I1, G6	
PZT 5A (Clevite)	365	25	1900	1 K	38	4.0	3.1	7.75	4.7×10^7	0.21	0.068	0.89	L1, C1	
PZT 4 (Clevite)	328	25	1400	1 K	30	3.7	3.0	7.5	3.2×10^8	0.26	0.087	2.2	L1, C1	
PZT HST-41 (Gulton)	270	25	1800	1 K	23	2	3.0	7.6	4.5×10^7	0.11	0.037	0.45	L2, G8	
5PbO·3GeO ₂	177	50	60	10 K	4.5	1				1.7			I2	
Gd ₂ (MoO ₄) ₃	161 ± 2	25	9-12	probably	0.2			4.6					K1, R1	Does not exhibit dielectric anomaly at Curie temp. Operates as a laser with Nd ³⁺ doping.
		100	10	1-10 K	0.15	0.1	2.1			1.0	0.48		U1, U2	Ferroelastic.
		143	9.8	"	0.1	0.14	2.1			1.4	0.67		C2, F1	
		151	10.0	"	0.01	0.25	2.1			2.5	1.2			
		159	9.7	"		4.9	8.7			50	5.8			
NaNbO ₃	160	25	8	1 K	7	0.4	2.0	2.1	$> 10^{11}$	5	2.5	> 6.3	S2, P1	ϵ practically constant to 140° C.

TABLE A-1. PYROELECTRIC MATERIALS CHARACTERISTICS (CONTINUED)

MATERIAL	Curie Temperature T_c °C	Temperature of Measurement T °C	Dielectric Constant ϵ	Frequency of Measurement F Hz	Polarization P_s $C \text{ cm}^{-2} \times 10^{-6}$	Pyroelectric Constant dP_g/dT $C \text{ cm}^{-2} \cdot ^\circ K^{-1} \times 10^{-8}$	Specific Heat c $J \text{ cm}^{-3} \cdot ^\circ K^{-1}$	Density ρ $g \text{ cm}^{-3}$	A.C. Resistivity (1 KHz) ρ $\Omega \cdot \text{cm}$	$(dP_g/dT) \cdot \epsilon^{-1}$ $\times 10^{-10}$	$(dP_g/dT) \cdot \rho^{1/2} \cdot \epsilon^{-1}$ $\times 10^{-4}$	Reference	COMMENTS
BaTiO ₃ (single crystal)	120	23 30 60 100	200	1 K	26 25.5 24 20	5 2 7 20	3.0	6	6×10^6	3.5	1.2×10^{-10}	P1, H1 C3	Absorbs 0.7 to 2 μ (I3) Cannot be fully poled (S3)
SBN, x = 0.52 (A)	115	25	380	1 K	29.2	6.5	2.1	5.2	1.6×10^8	1.7	0.81	G3, G4	Transmits 0.5-6.0 μ (B5)
SBN, x = 0.33	62	25	1800	1 K	23.3	11			1.2×10^8	0.61	0.29	B1	
SBN, x = 0.25	47	25	5000	1 K	18	31			7.1×10^6	0.62	0.29		
NH ₄ IO ₃	85	26	30	1 K		0.3		3.3	2.9×10^8	1		C4	Transmits 0.35 to 2 μ . Explodes above 180°C.
TGFB (B)	73	25 50	11 20	10 K 10 K	3.7 3.1	1.3 4.5	2.6 3.1	1.66		12 22	4.6 7.1	W1, S4 H2	
DTGS (C)	62.9	25 50	20 80	1 K 1 K	2.6 1.8	2.5 7.5	(2.5)	(1.7)	5×10^{10}	12 9.4	4.8 3.8	S5, B3 B4	T_c depends on D ₂ substitution for H ₂ . Only a maximum of 64.8% possible.
TGS _{0.67} TGFB _{0.33}	59.9	25 50	(35)	1 K	2.9 1.75	3.0 8.2	(2.5)	(1.66)		9	3.4	B6	TGS:TGFB ratio can be varied to vary T_c
KTN (D)	54	25 40	900 2500	800 800	9.3 8.4	2 20				0.22 1.3		A1	Transmits out to 6 μ . KTaO ₃ and KNbO ₃ form solid solution. Parameters depend on composition (C6, T1)
TGS (E)	49	10 25 40	35 50 150	1 K 1 K 1 K	3.0 2.75 2.0	1.5 3.5 11	2.4 2.5 2.8	1.65-1.68	1.8×10^{10}	4.4 7.0 7.3	1.8 2.8 2.6	P1, D1 S6, C5 K2	Absorbs below 0.24 μ (S9) and between 2 to > 400 μ (M2). Transmits 0.25-1.8 μ . Loss tan. increases below ambient with decreasing temp. (I4). Doping, X-ray, and U. V. irradiation affect parameters (Z1, H3, W6, Y2, Y3, S9).

TABLE A-1. PYROELECTRIC MATERIALS CHARACTERISTICS (CONTINUED)

MATERIAL	Curie Temperature T_c °C	Temperature of Measurement T °C	Dielectric Constant ϵ	Frequency of Measurement F Hz	Spontaneous Polarization P_s $C\text{ cm}^{-2} \times 10^{-6}$	Pyroelectric Constant dP_s/dT $C\text{ cm}^{-2}\text{ }^\circ\text{K}^{-1} \times 10^{-8}$	Specific Heat c $J\text{ cm}^{-3}\text{ }^\circ\text{K}^{-1}$	Density s $g\text{ cm}^{-3}$	A.C. Resistivity (1 KHz) ρ $\Omega\text{-cm}$	$(dP_s/dT) \epsilon^{-1}$ $\times 10^{-10}$	$(dP_s/dT) (\epsilon \times 10^{-10})^{-1}$	$(dP_s/dT) \rho^{1/2} \epsilon^{-1}$ $\times 10^{-4}$	Reference	COMMENTS
TGS/Se (~15%Se) + additive	49	25	28	10 K		5	2.5		4×10^9	17.8	7.1	12.7	P2	Mullard (U. K.) Development; Material does not depole.
TGS/Se (~5%Se)	47	25	26	10 K		4.1	2.5		5×10^9	15.8	6.3	11.7	P2	Mullard (U. K.) Development; Material does not depole.
DTGSe (F)	34.5	25	(100)		3.2	7.5	(2.3)			7.5	3.3		M3	Will operate up to 95% relative humidity (C1). Has rather flat response over a wide temp. range (B1, N3).
TGSe (G)	22.2	0 15	(100)		3.0 2.6	13	2.1 2.3			13	5.7		H2, M3, S7, S8, G7	
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	(M)	25 50	10.3 (10)	1 K	0.8 1	0.82	2.06			7.8 (10)	9.5 (12)		L1, A2 W2	
$\text{Li}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$		20 79				0.57 0.65							A2	
Polyvinylidene fluoride (CH_2CF_n)	not known, softens at 150°C melts at 177°C	25	11		2	0.24			6.7×10^9	2.2	0.9	0.82	B2, G5	Transmits 0.4-2 μ absorbs 3-300 μ . T_c (if it exists) may be near the melting point (N2)

TABLE A-1. PYROELECTRIC MATERIALS CHARACTERISTICS (CONTINUED)

MATERIAL	Curie Temperature T_c °C	Temperature of Measurement T °C	Dielectric Constant ϵ	Frequency of Measurement F Hz	Spontaneous Polarization P_s $C \text{ cm}^{-2} \times 10^{-6}$	Pyroelectric Constant dP_s/dT $C \text{ cm}^{-2} \text{ K}^{-1} \times 10^{-8}$	Specific Heat c $J \text{ cm}^{-3} \text{ }^\circ\text{K}^{-1}$	Density ρ g cm^{-3}	A.C. Resistivity (1 KHz) ρ $\Omega \text{ cm}$	$(dP_s/dT) \epsilon^{-1}$ $\times 10^{-10}$	$(dP_s/dT) \rho^{1/2} \epsilon^{-1}$ $\times 10^{-4}$	Reference	COMMENTS
SBSI	22	0 10 15	2200 2500 3000		22 15 12	60 100	2.38	8.2				F2 W2	Also photoconductive (U3)
GASH (H)	(M)	25	6	1 K	0.35	0.15	~ 1		9×10^{10}	2.5	4.5	H4, P1, N3	Ge isomorph (for Al) SeO ₄ isomorph (for SO ₄) (Ge and SeO ₄) isomorph (for Al and SO ₄). Similar performance (H4).
GUL (I)		25	4.6	1 K		0.62	~ 1.5		4×10^{11}	13.5	26	P1	
EDT (I)		25	7.0	1 K		0.2	~ 1		$> 10^{11}$	3	> 6	P1	dP_s/dT is constant from 20° to 80°C (N3)
Colemanite (K)	-7	-10 -20	60 12	1 K 1 K	0.29 0.46	5.4 1.2	0.58	2.42		9 10	15.5 17	W3, C7	Depending on purity, T_c of 2.5°C is also reported (D2). Synthetic strontium isomorphs (polycrystalline) have been grown (W4, W5).
KDDP (I)	-50±2	-60	50	1 K	4.0	10		2.36	8.6×10^7	20		M4, A3	Transmits 0.2 to 2μ.
(NH ₂ CH ₂ COOH) HNO ₃	-67	-77 -190	50 15	10 K 10 K	0.6 1.5	5 0.13	2.0	1.58		10 0.87	5	P3	
CS(NH ₂) ₂ (Thiourea)	-104	-178	400		3.4	1		1.40		0.25		G9	
KH ₂ PO ₄ (KDP)	-150	-178	2500	1K	4.8	3.3	0.94	2.34	7.2×10^6	0.13	1	B7, A3, D3, K3, S10	Transmits 0.2 to 2μ.

TABLE A-1. PYROELECTRIC MATERIALS CHARACTERISTICS (CONTINUED)

NOTES

Values in parentheses are based on assumptions.

A	SBN = $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$
B	TGFB = $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{BeF}_4$
C	DTGS = $(\text{ND}_2\text{CH}_2\text{COOD})_3\text{D}_2\text{SO}_4$
D	KTN = $\text{KTa}_{0.57}\text{Nb}_{0.43}\text{O}_3$
E	TGS = $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$
F	DTGSe = $(\text{ND}_2\text{CH}_2\text{COOH})_3\text{D}_2\text{SeO}_4$
G	TGSe = $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SeO}_4$
H	GASH = $(\text{CN}_3\text{H}_6\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$
I	GUL = Glucuronolactone = $\text{CO} \cdot (\text{CHOH})_2 \cdot \text{CH}(\text{O}) \cdot \text{CHOH} \cdot \text{CHO}$
J	EDT = $\text{C}_2\text{H}_4(\text{NH}_3)_2\text{C}_4\text{H}_4\text{O}_6$
K	Colemanite = $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
L	KDP = KD_2PO_4 (~90%D ₂)
M	Decomposes before T_c can be measured.

APPENDIX B - MEASURED DATA ON SELECTED PYROELECTRIC MATERIALS -
OPTICAL TRANSMISSION - OPTICAL REFLECTANCE

TGFB

DTGS

$\text{TGS}_{0.88} - \text{TGFB}_{0.12}$

TGS

$\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$

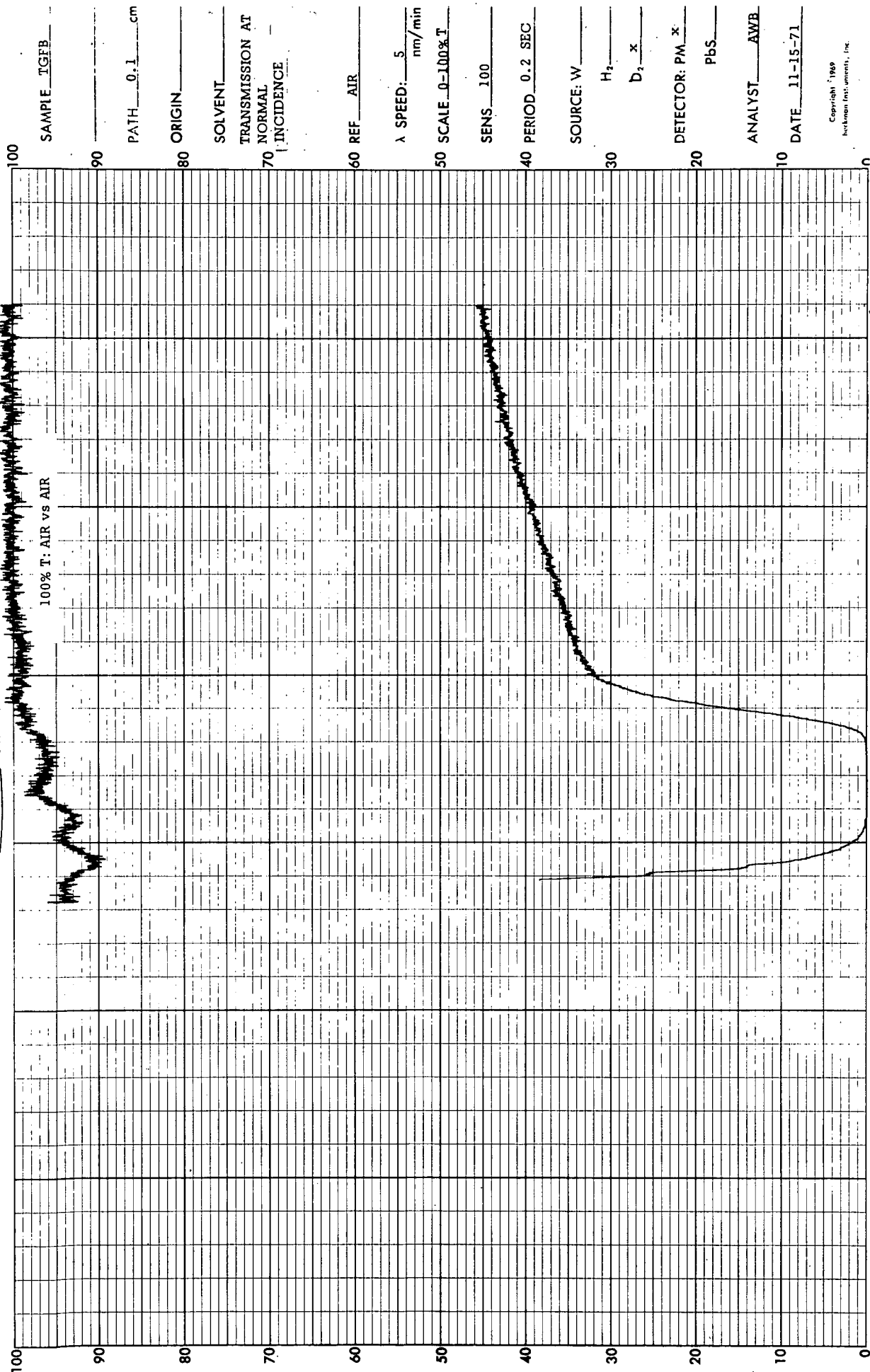
Polyvinylidene Fluoride

Beckman

DK-2 CHAR1

WHEN REORDERING SPECIFY CHART NO. 566402

BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE TGFB

90

PATH 0.1 cm

80

SOLVENT

TRANSMISSION AT

70 NORMAL

INCIDENCE

60 REF AIR

λ SPEED: 5 nm/min

50 SCALE 0-100%T

SENS 100

40 PERIOD 0.2 SEC

SOURCE: W

30 H₂

D₂ x

DETECTOR: PM x

20 PbS

ANALYST AWB

10 DATE 11-15-71

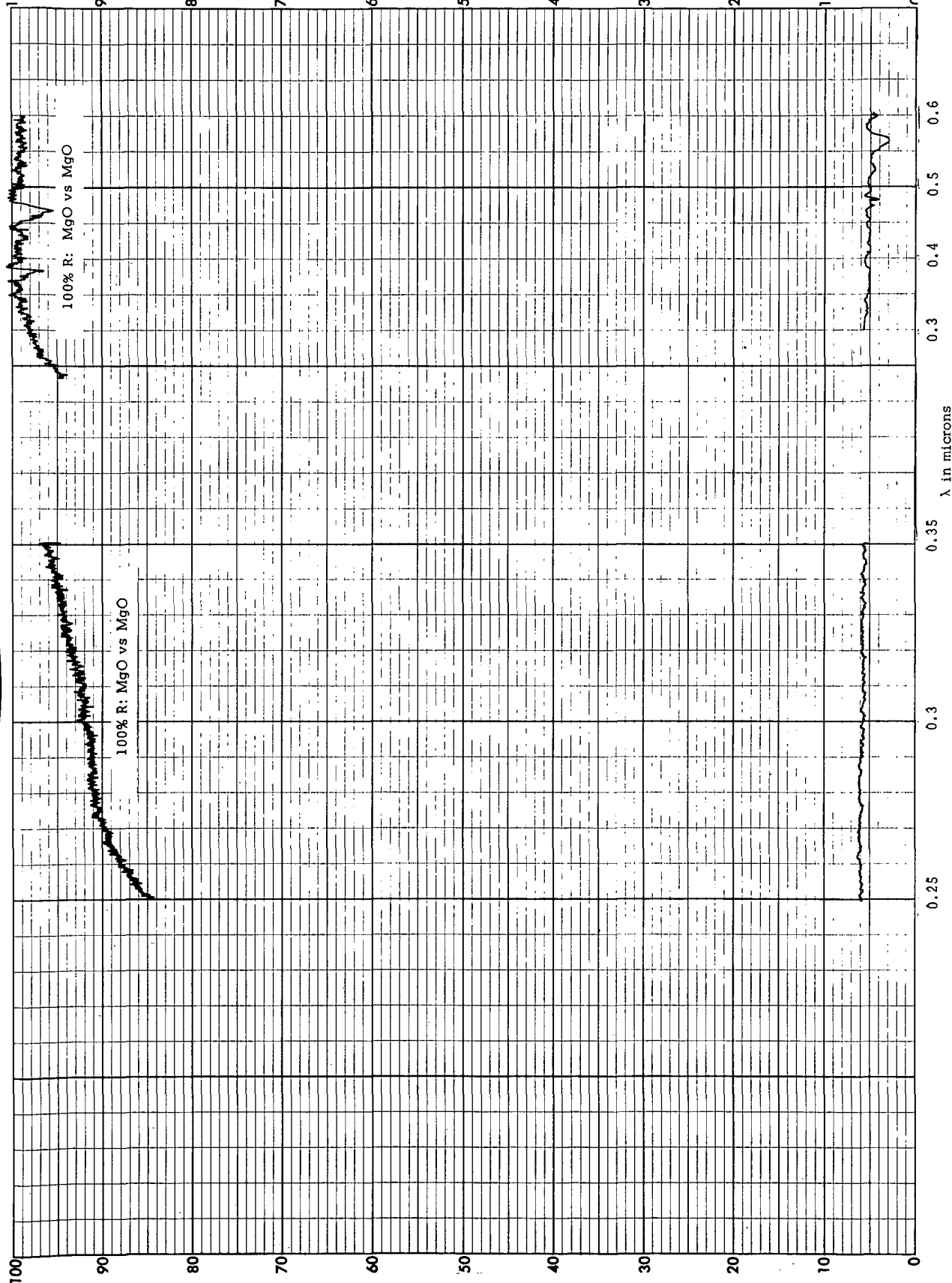
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Beckman DK-2 CHART

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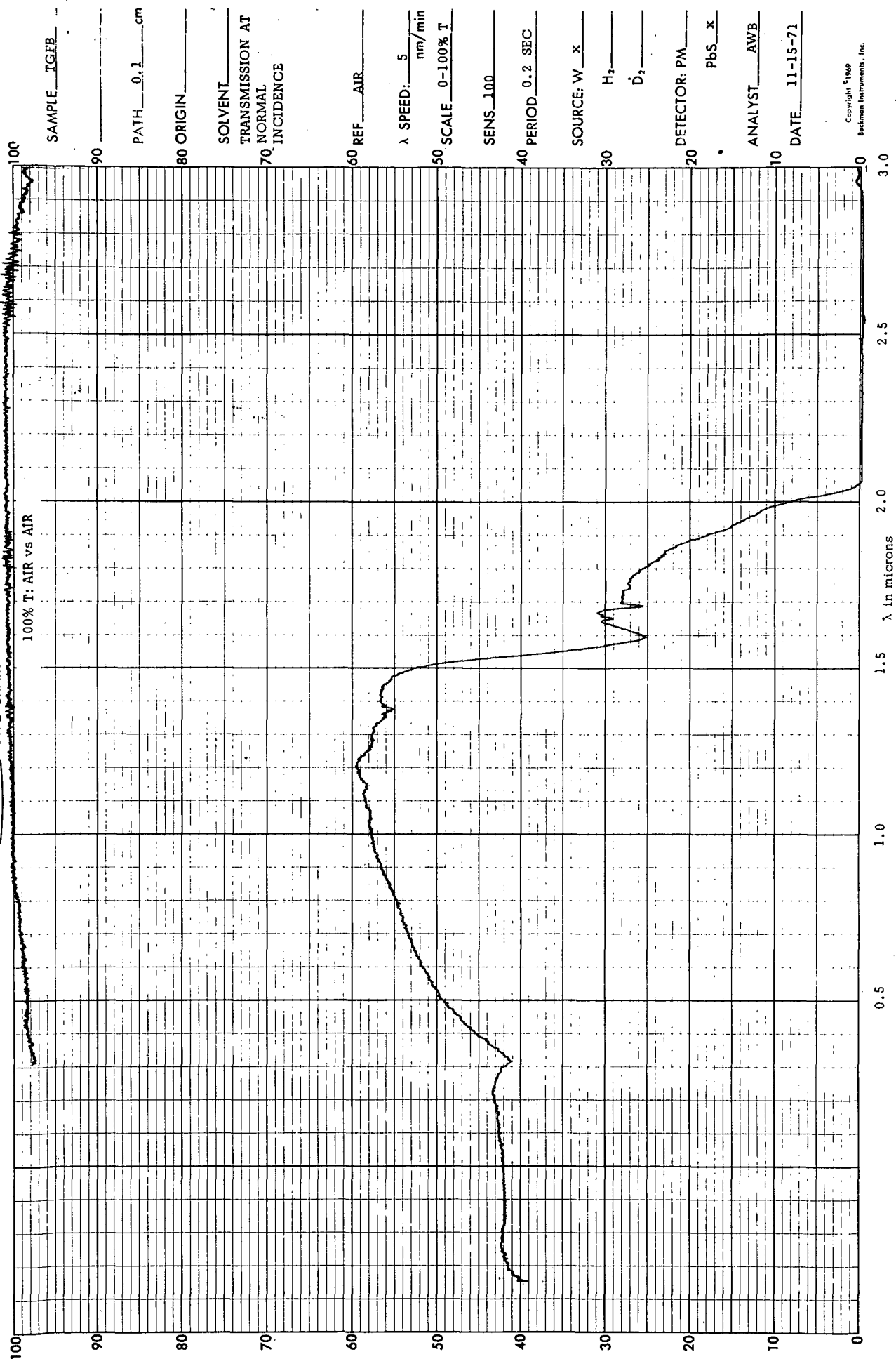
SAMPLE TGFB
 PATH 0.1 cm
 80 ORIGIN
 SOLVENT
 DK-2 REFLECTANCE
 70 AT 5° INCIDENCE
 60 REF MgO
 λ SPEED: 5 nm/min
 50 SCALE 0-100%
 SENS 150
 40 PERIOD 0.6 SEC
 SOURCE: W
 30 H₂
 D₂ x
 20 DETECTOR: PM x
 PbS
 ANALYST AWB
 10 DATE 11-15-71



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WHEN ORDERING SPECIFY CHART NO. 566402

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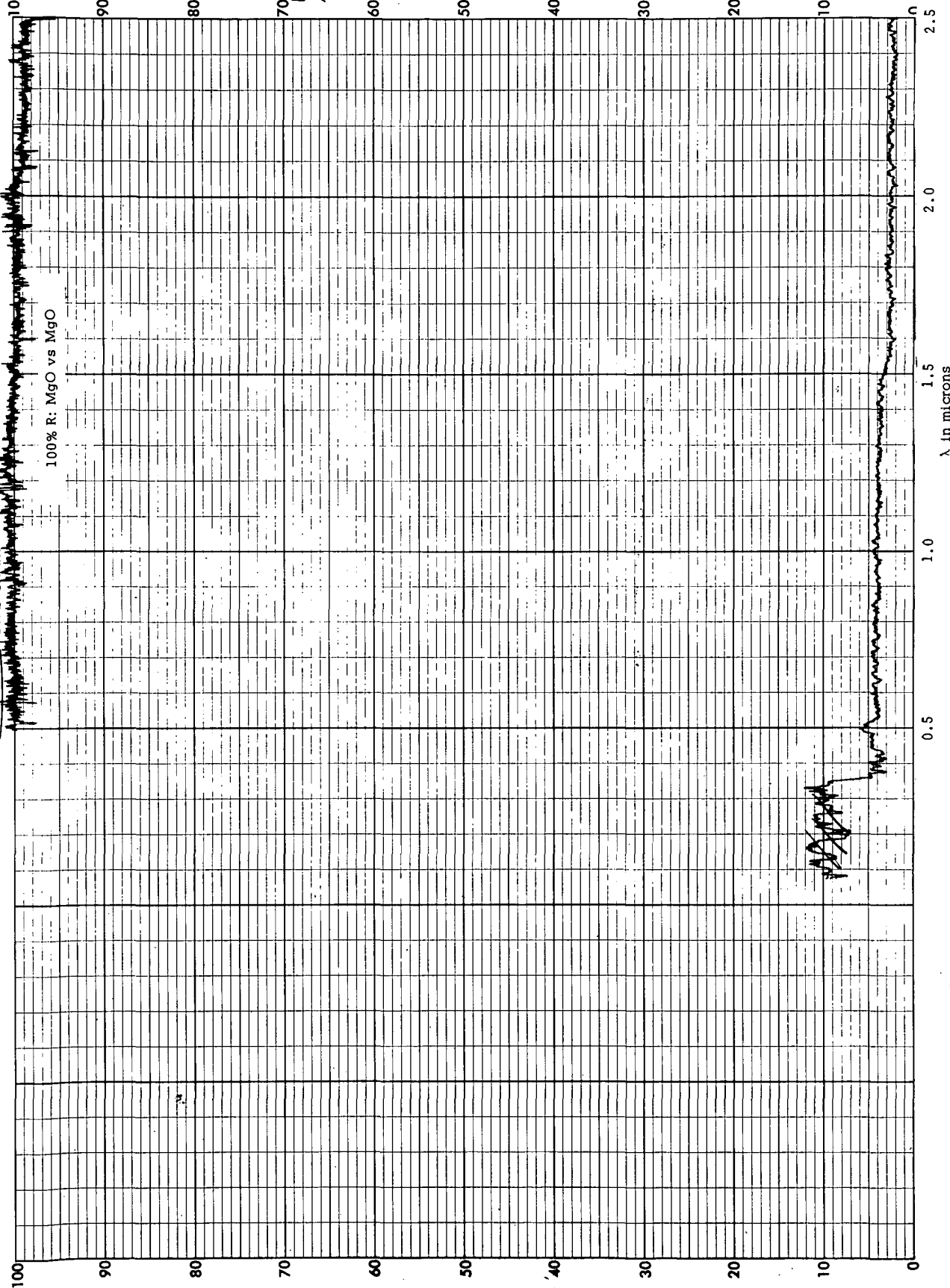


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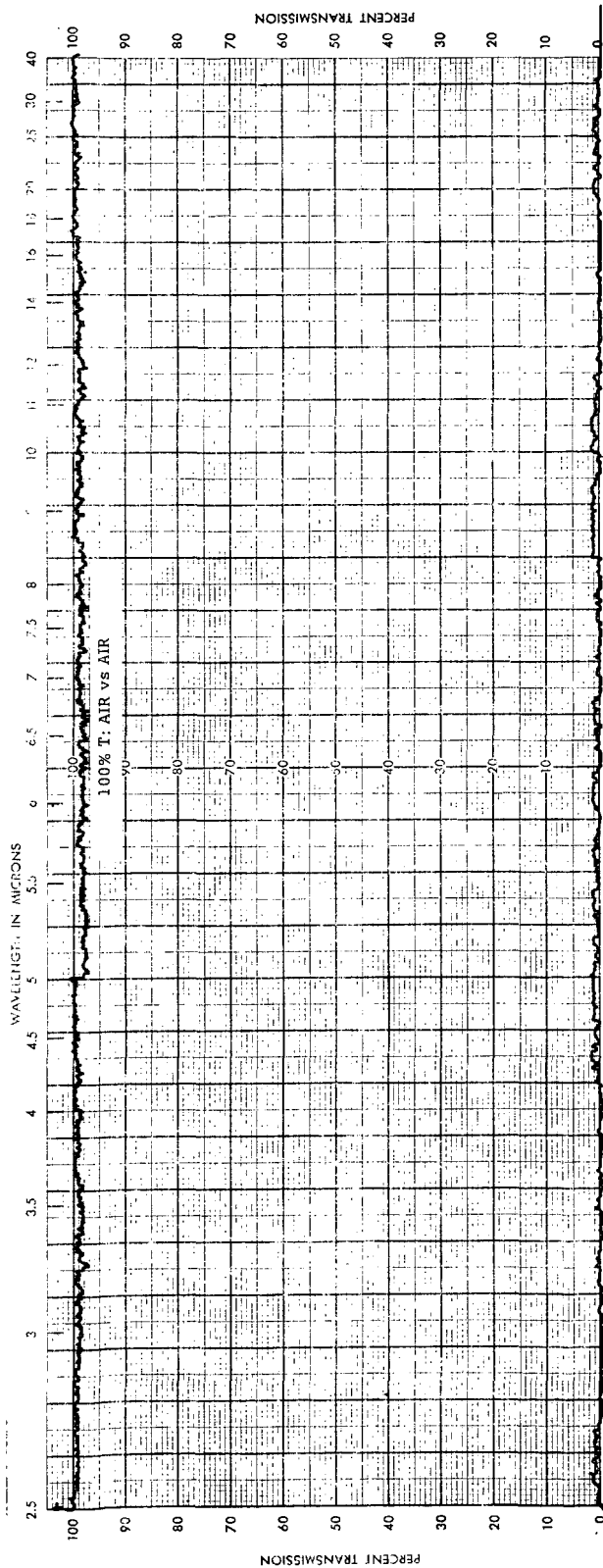
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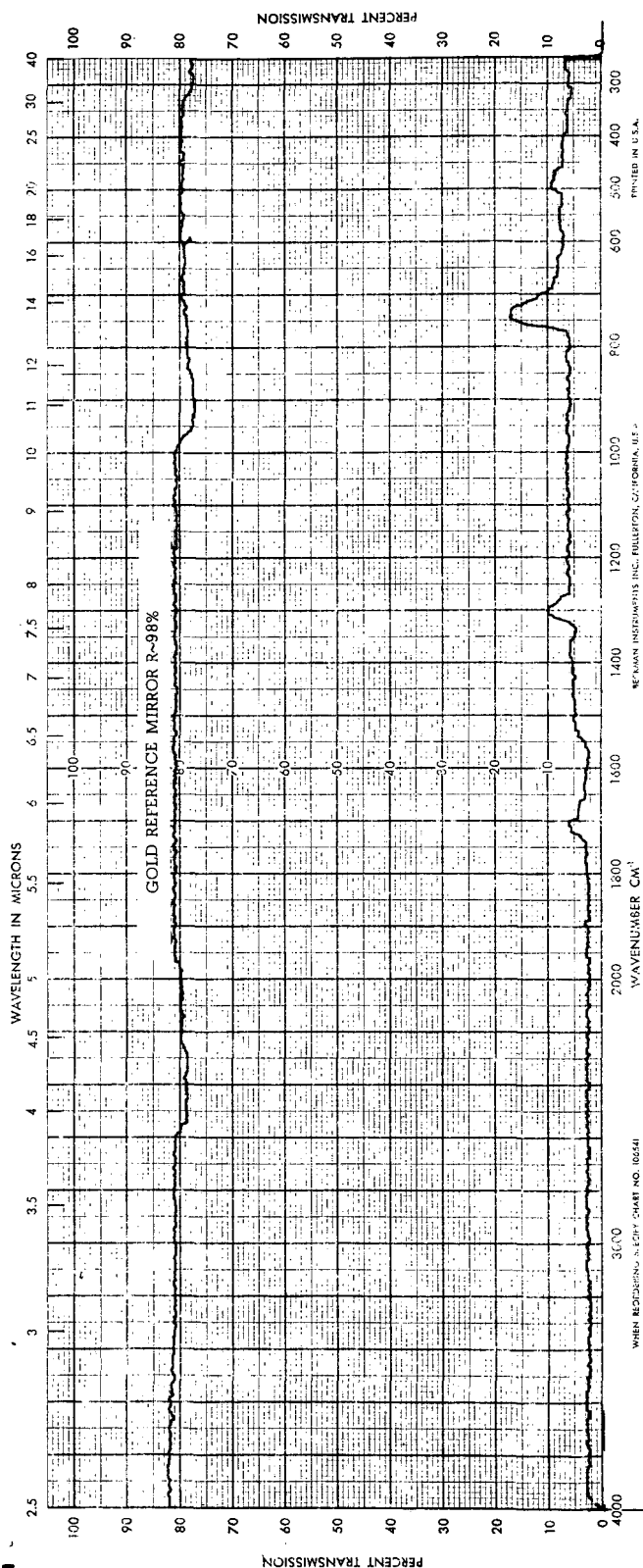
SAMPLE TGFB
 PATH 0.1 cm
 ORIGIN _____
 SOLVENT _____
 DK-2 REFLECTANCE
 AT 5° INCIDENCE
 60 REF MgO
 λ SPEED: 5 nm/min
 50 SCALE 0-100%
 SENS 150
 40 PERIOD 0.2 SEC
 SOURCE: W x
 H₂ _____
 D₂ _____
 DETECTOR: PM _____
 PbS x
 ANALYST AWB
 DATE 11-15-71



SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE TGFB
 SOURCE BEC
 STRUCTURE
 IR-20 TRANSMISSION
 AT NORMAL INCIDENCE
 PATH 1 mm
 SOLVENT
 CONCENTRATION
 PHASE
 COMMENTS
 ANALYST AWB
Beckman®



SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE TGFB
 SOURCE
 STRUCTURE
 IR-20 SPECULAR REFLECTANCE
 AT 30° INCIDENCE
 PATH 1 mm
 SOLVENT
 CONCENTRATION
 PHASE
 COMMENTS
 ANALYST AWB
Beckman®



Beckman

DK-2 CHART

WHEN RECORDING SPECIFY CHART NO. 566402

BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE DTGS

90

PATH 0.1 cm

80 ORIGIN

SOLVENT

TRANSMISSION AT

NORMAL

70 INCIDENCE

60 REF AIR

λ SPEED: 5

nm/min

50 SCALE 0-100% T

SENS 100

40 PERIOD 0.2 SEC

SOURCE: W

30 H₂

D₂ X

20 DETECTOR: PM X

PBS

ANALYST AWB

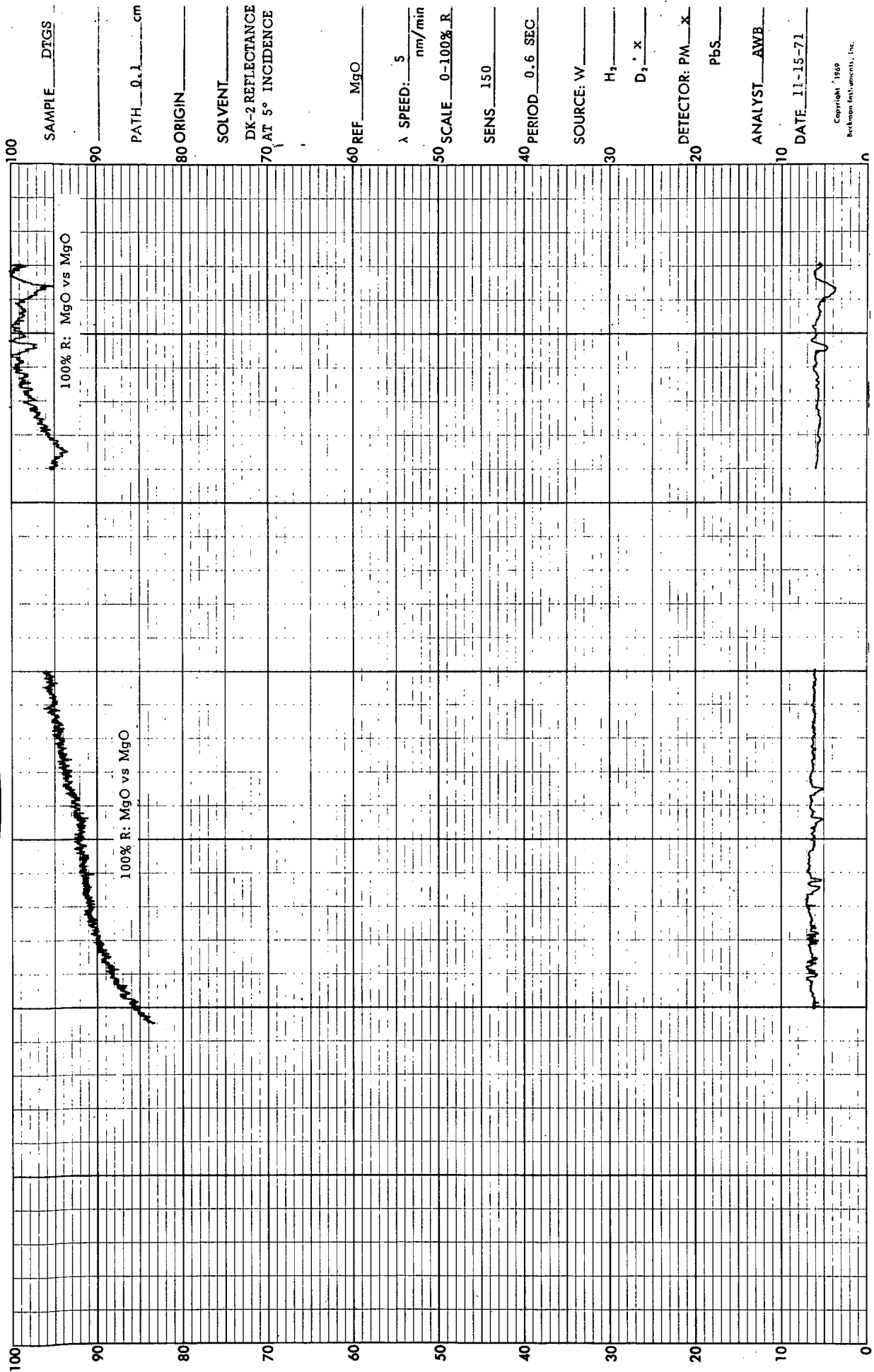
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Beckman DK-2 CHART

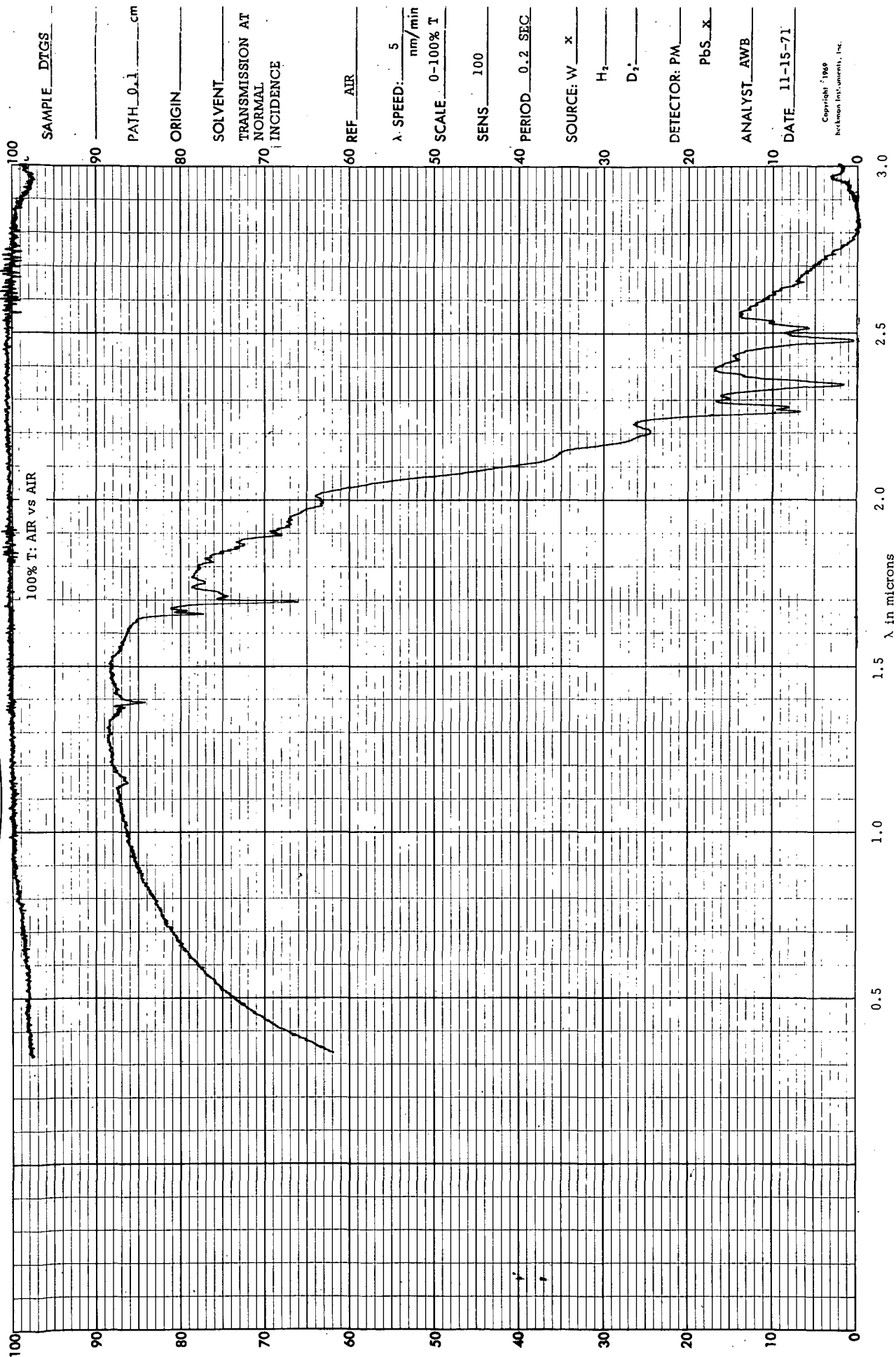
WHEN REORDERING SPECIFY CHART NO. 566402 BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



Beckman DK-2 CHART

WHEN REORDERING SPECIFY CHART NO. 566402

BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE DTGS

90

PATH 0.1 cm

80

ORIGIN

SOLVENT

TRANSMISSION AT
NORMAL
INCIDENCE

70

60 REF AIR

λ SPEED: 5
nm/min

50 SCALE 0-100% T

SENS 100

40 PERIOD 0.2 SEC

SOURCE: W x

30

H₂

D₂

DETECTOR: PM

20

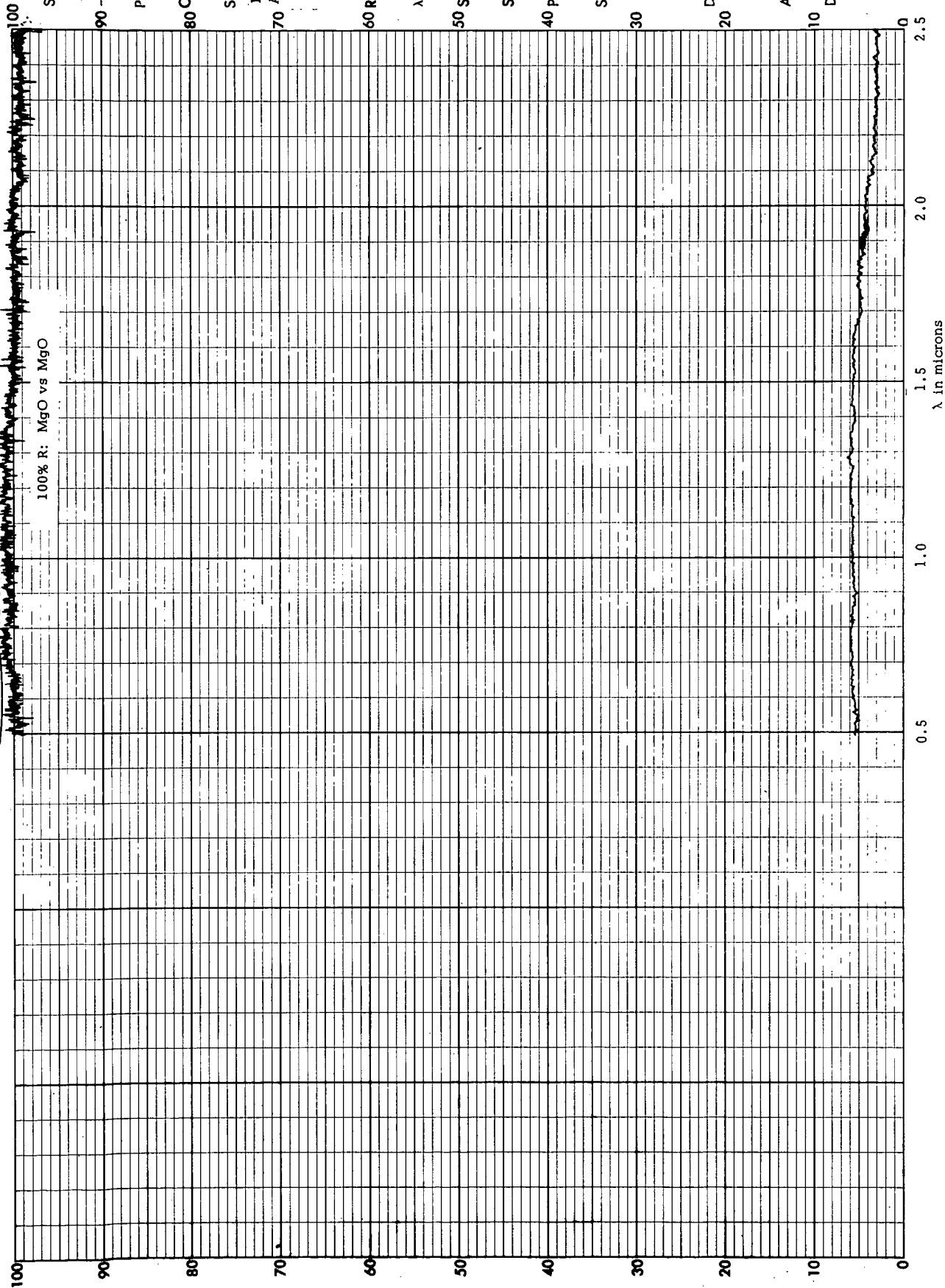
PbS x

ANALYST AWB

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B-9



SAMPLE DTGS

90

PATH 0.1 cm

80 ORIGIN

SOLVENT

DK-2 REFLECTANCE
70 AT 5° INCIDENCE

60 REF MgO

λ SPEED: 5
nm/min

50 SCALE 0-100% R

SENS 150

40 PERIOD 0.2SEC

SOURCE: W x

30 H₂

D₂

DETECTOR: PM

20

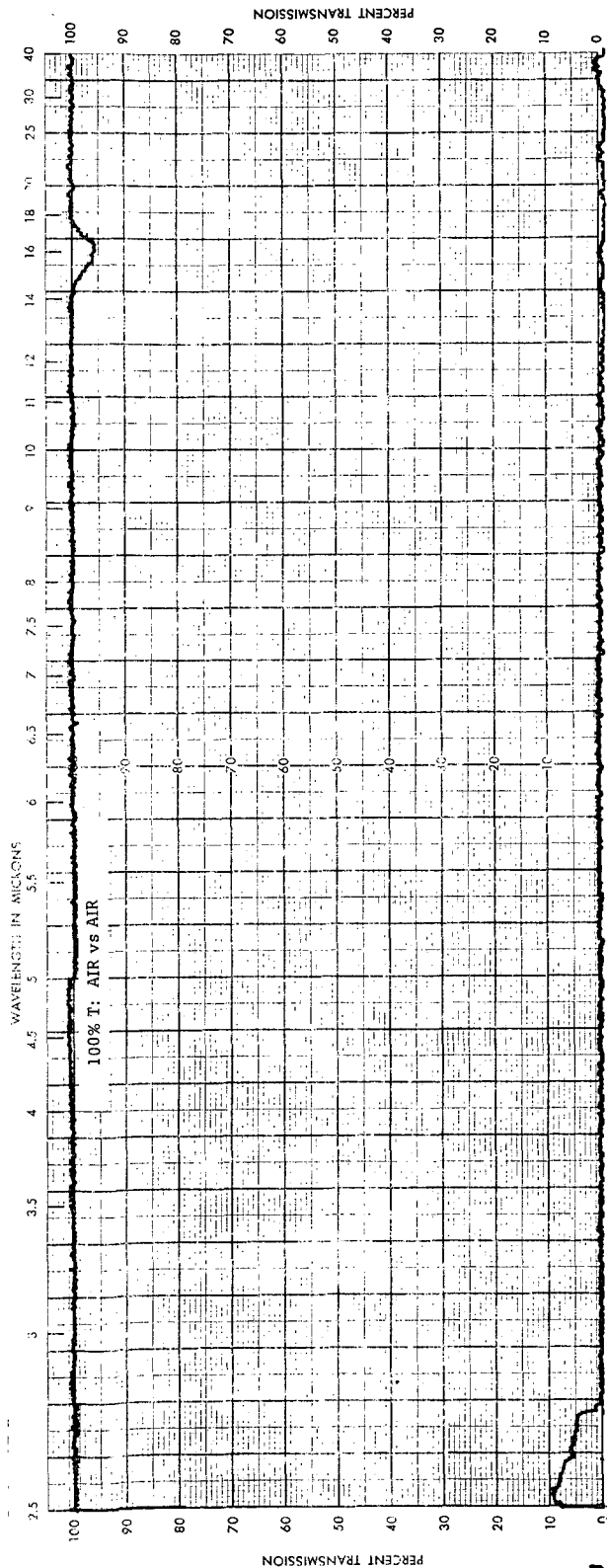
PbS x

ANALYST AWB

10 DATE 11-15-71

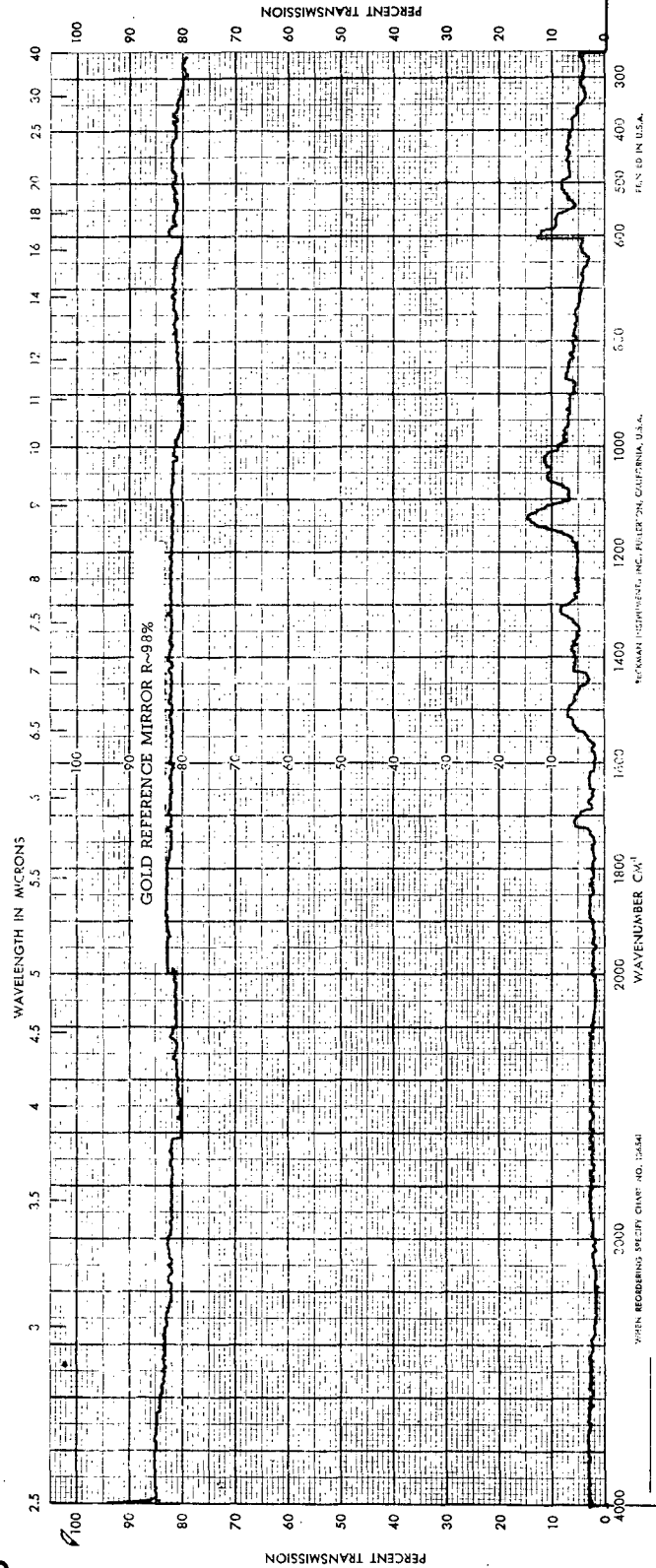
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SPECTRUM NO. _____
 DATE _____
 SAMPLE DTGS _____
 SOURCE BEC _____
 STRUCTURE _____
 IR-20 TRANSMISSION
 AT NORMAL INCIDENCE
 PATH 1 mm _____
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB _____
Beckman®



B-10

SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE DTGS _____
 SOURCE BEC _____
 STRUCTURE _____
 IR-20 SPECULAR
 REFLECTANCE AT
 30° INCIDENCE
 PATH 1 mm _____
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB _____
Beckman®

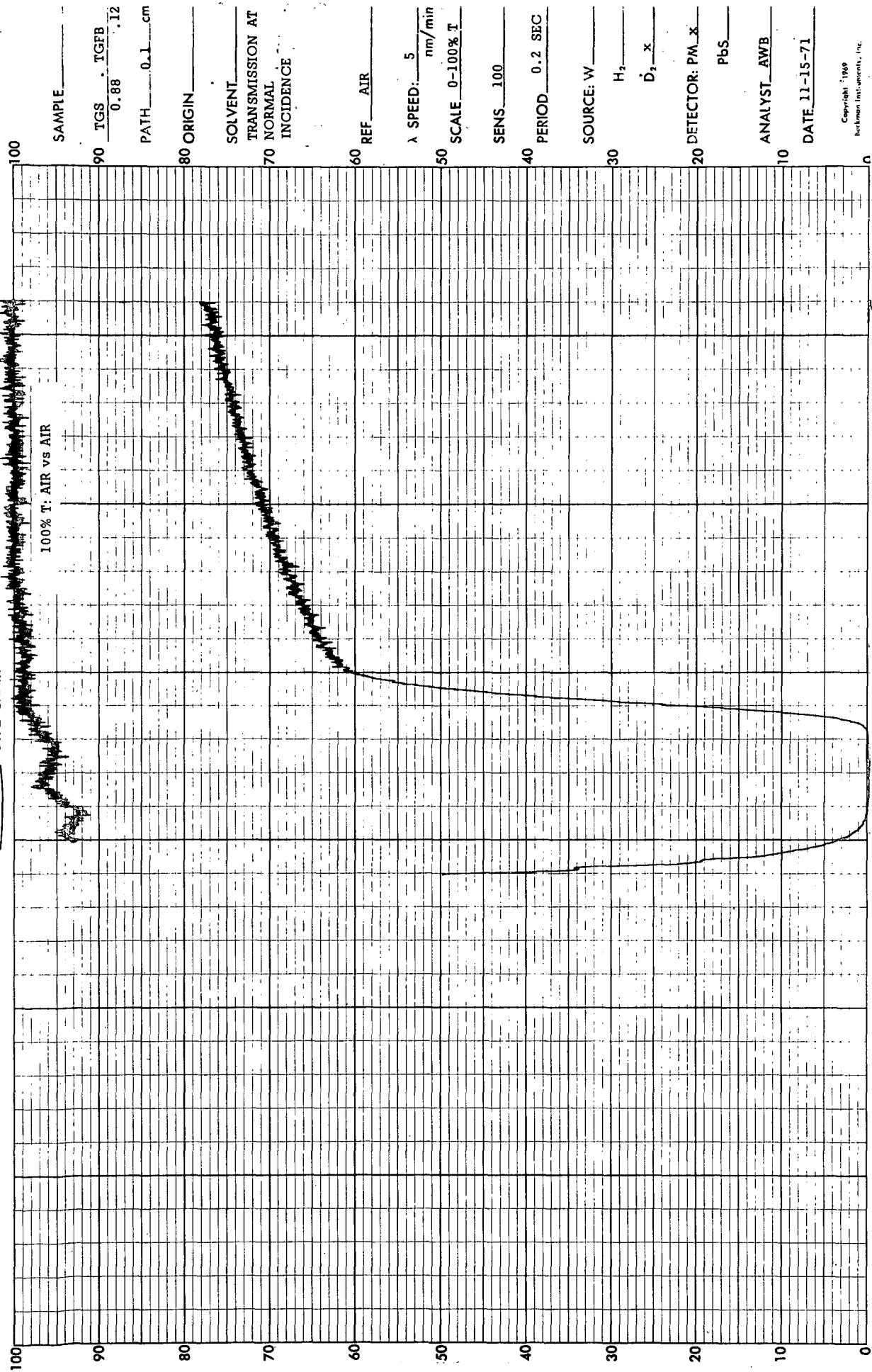


Beckman

DK-2 CHART

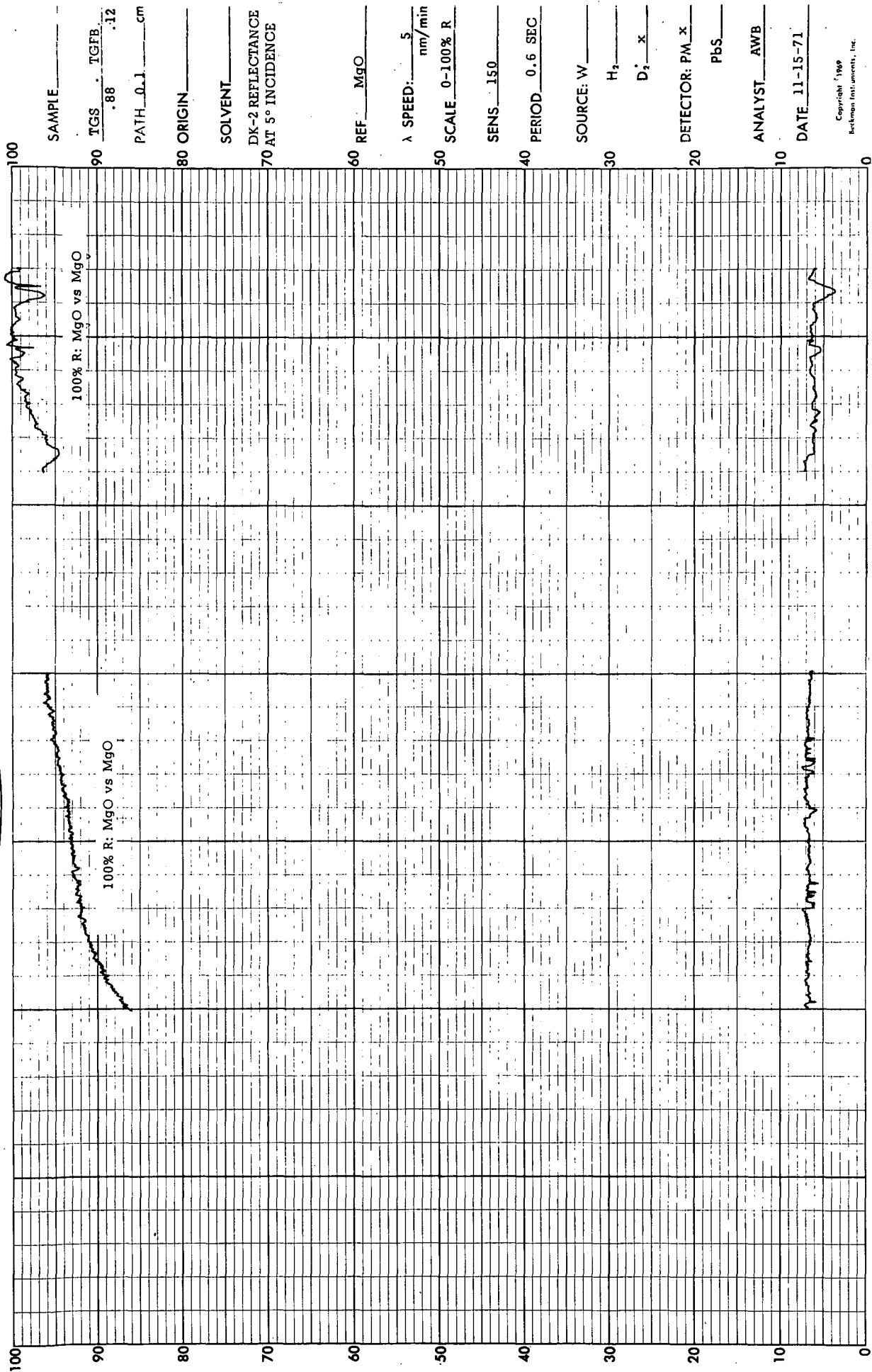
WHEN REORDERING SPECIFY CHART NO. 566402

BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE _____
 90 TGS - TGFB
 0.88
 .12
 PATH 0.1 cm
 80 ORIGIN _____
 SOLVENT _____
 TRANSMISSION AT
 70 NORMAL
 INCIDENCE
 60 REF AIR
 λ SPEED: 5 nm/min
 50 SCALE 0-100% T
 SENS 100
 40 PERIOD 0.2 SEC
 SOURCE: W _____
 H₂ _____
 D₂ x _____
 30
 20 DETECTOR: PM x
 PbS
 10 ANALYST AWB
 DATE 11-15-71

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SAMPLE _____

90 TGS .88 TGF .12

PATH 0.1 cm

80 ORIGIN _____

SOLVENT _____

DK-2 REFLECTANCE
70 AT 5° INCIDENCE

60 REF MgO _____

λ SPEED: 5
nm/min

50 SCALE 0-100% R

SENS 150

40 PERIOD 0.6 SEC

SOURCE: W _____

30 H₁ _____

D₁ x

20 DETECTOR: PM x

PBS

ANALYST AWB

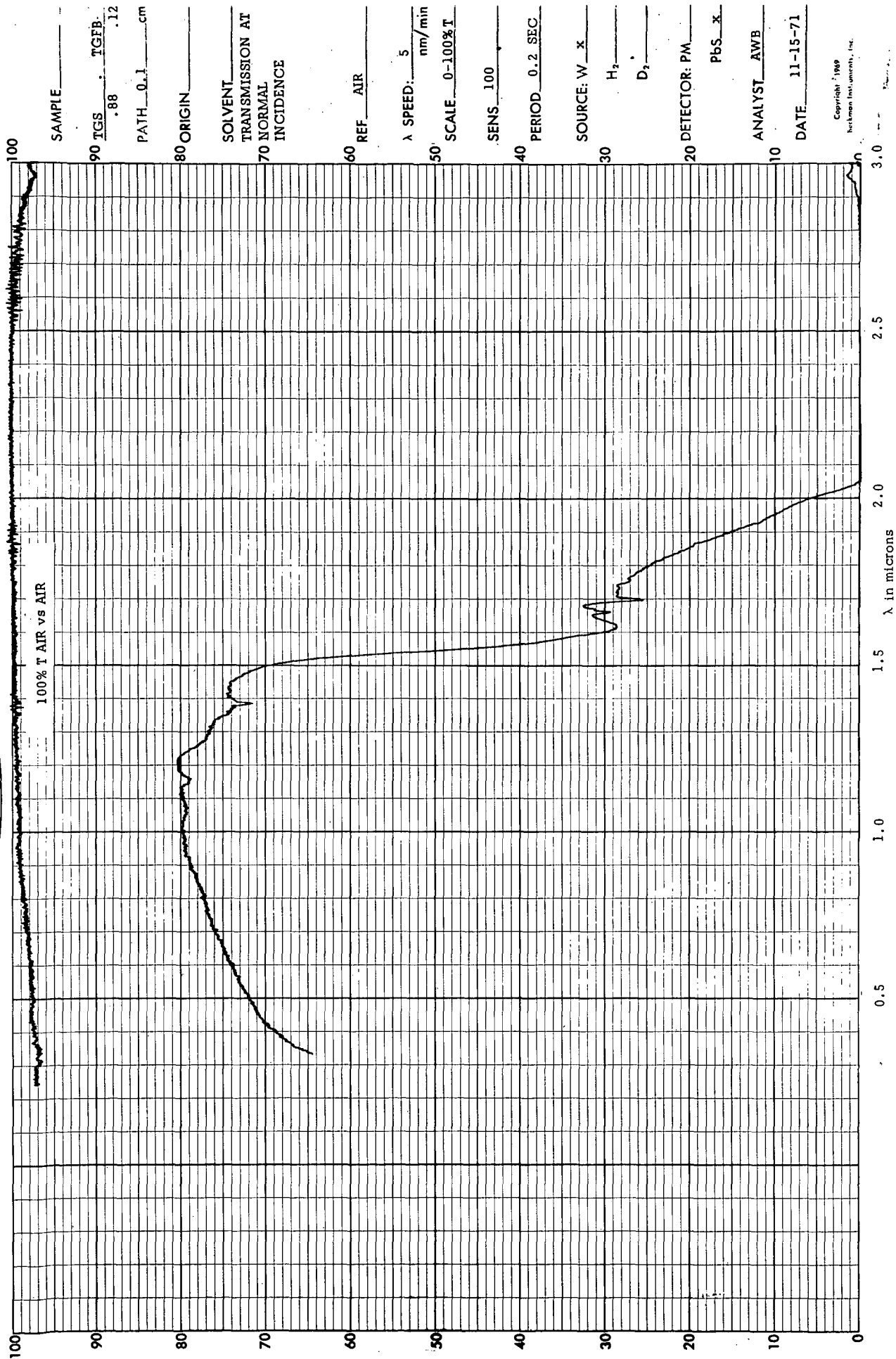
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BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE

90 TGS .88 TGF .12

PATH 0.1 cm

80 ORIGIN

SOLVENT
TRANSMISSION AT
70 NORMAL
INCIDENCE

60 REF AIR

λ SPEED: 5 nm/min

SCALE 0-100% T

SENS 100

PERIOD 0.2 SEC

SOURCE: W x

H₂

D₂

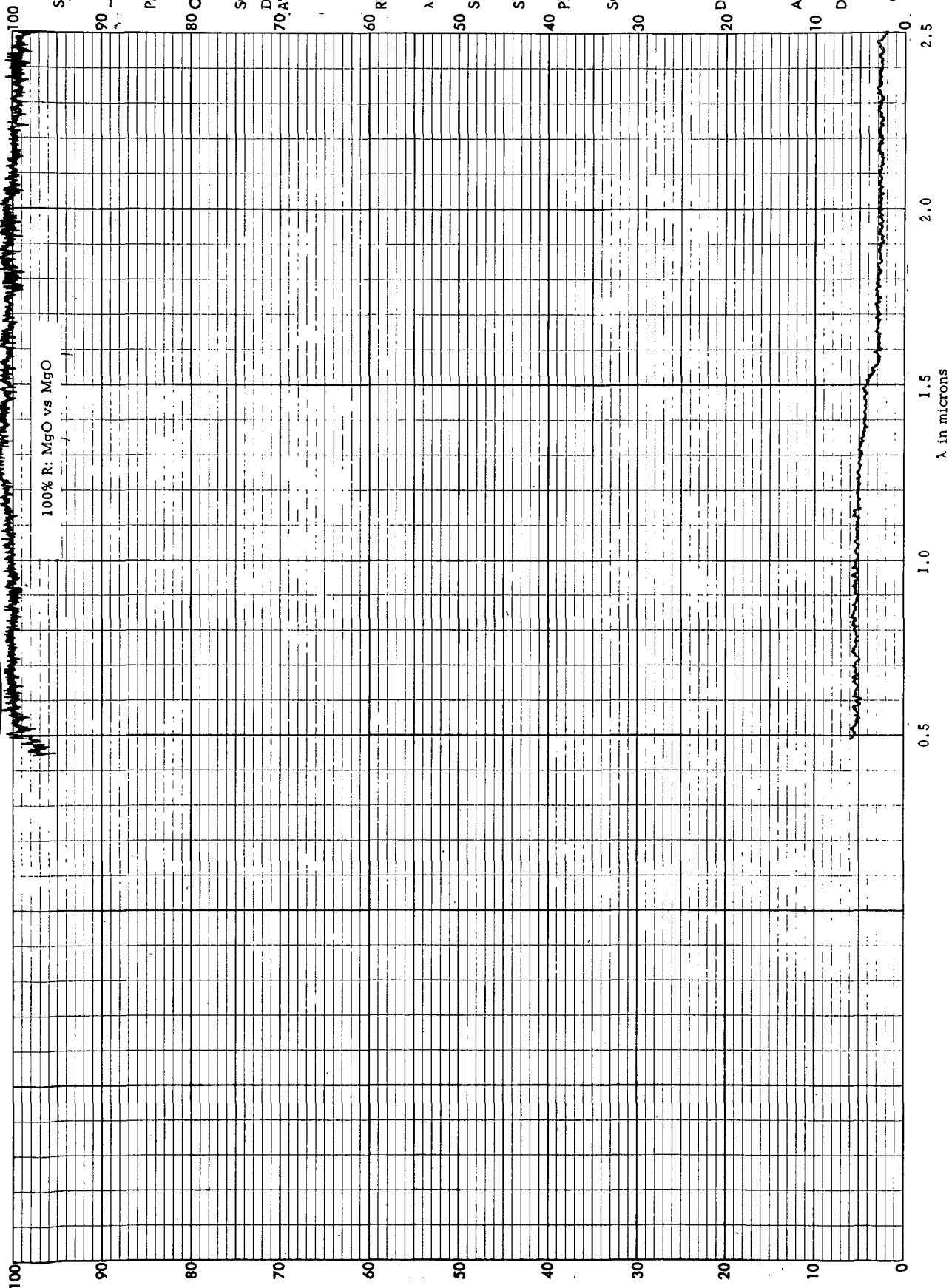
20 DETECTOR: PM

PbS x

ANALYST AWB

DATE 11-15-71

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100% R: MgO vs MgO

SAMPLE _____
90 TGS .88 TGPB .12
PATH 0.1 cm

80 ORIGIN _____
SOLVENT _____
DK-2 REFLECTANCE
70 AT 5° INCIDENCE

60 REF MgO _____

λ SPEED: 5 nm/min

SCALE 0-100%R

SENS 150

PERIOD 0.2 SEC

SOURCE: W x

H₂ _____

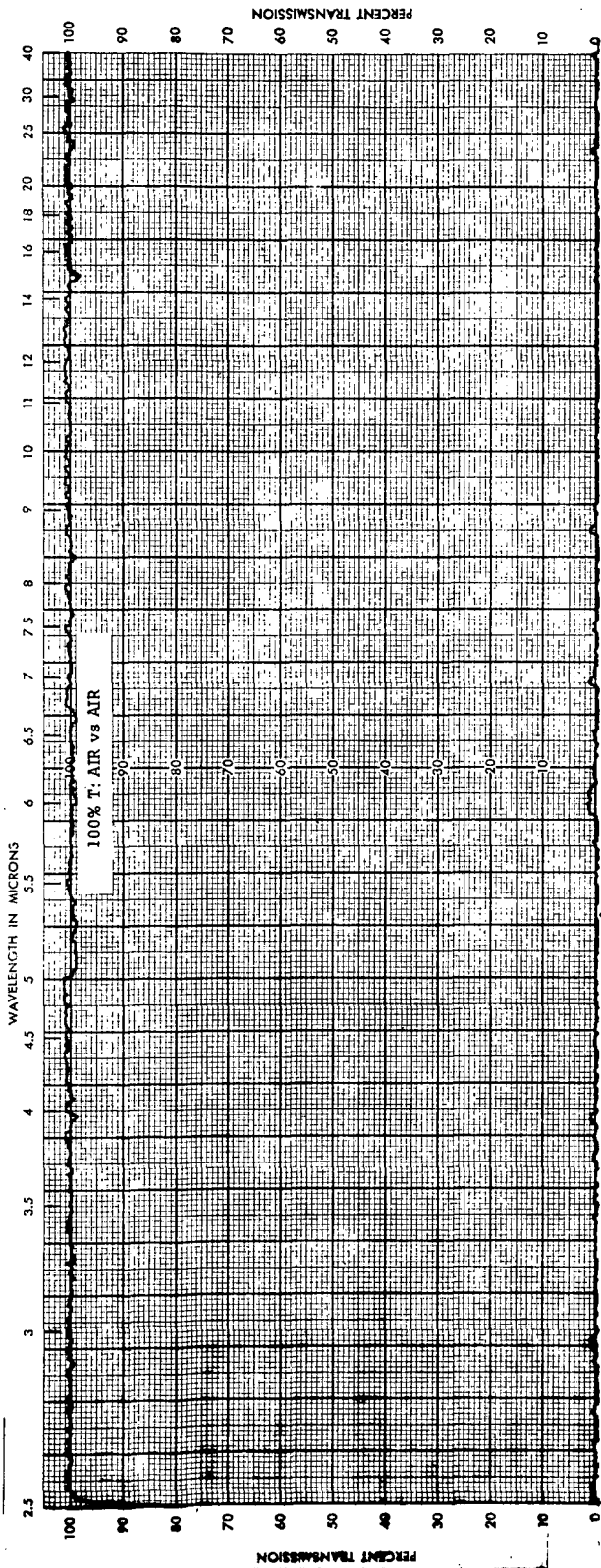
D₂ _____

20 DETECTOR: PM

PbS x

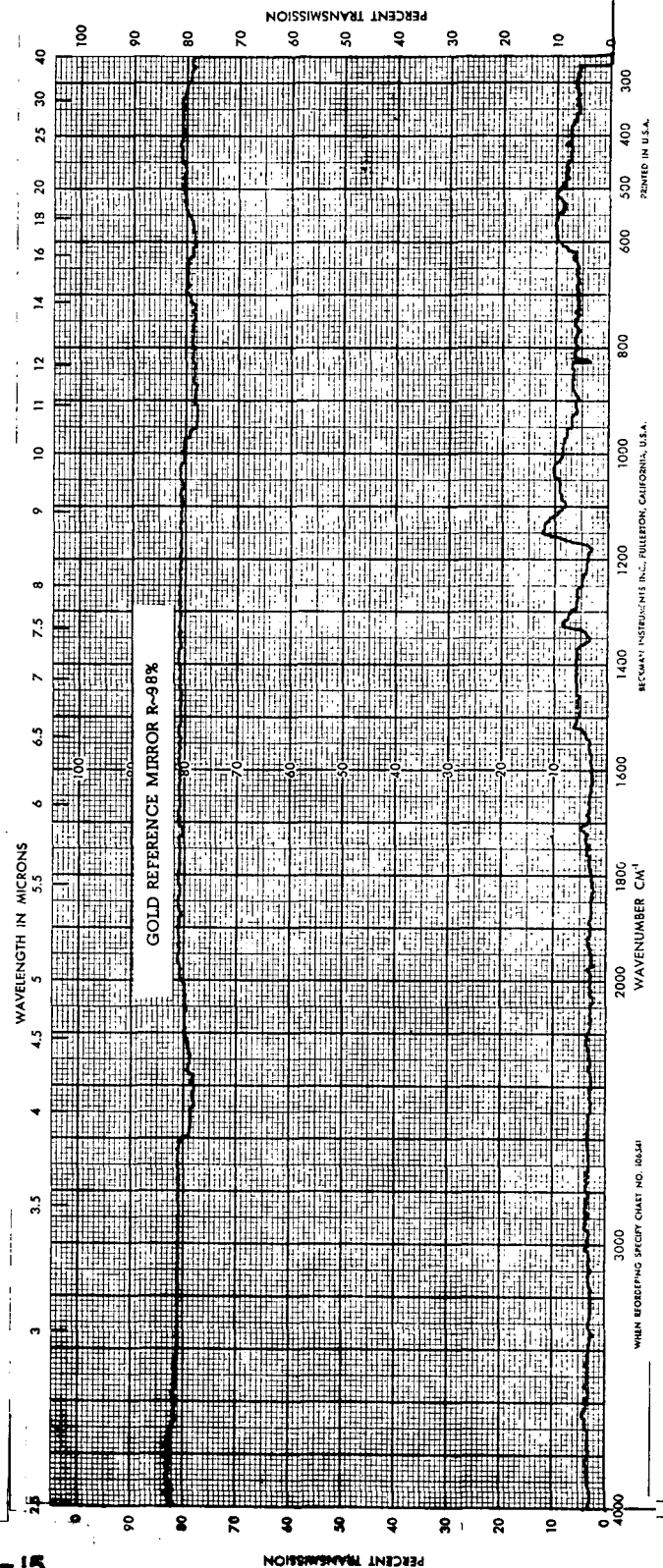
ANALYST AWB

DATE 11-15-71



SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE TGS 88 12
 SOURCE REC
 STRUCTURE _____
 IR-20 TRANSMISSION AT
 NORMAL INCIDENCE
 PATH 1 mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB
Beckman®

15-B



SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE TGS 88 12
 SOURCE REC
 STRUCTURE _____
 IR-20 SPECULAR
 REFLECTANCE AT
 30° INCIDENCE
 PATH 1 mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB
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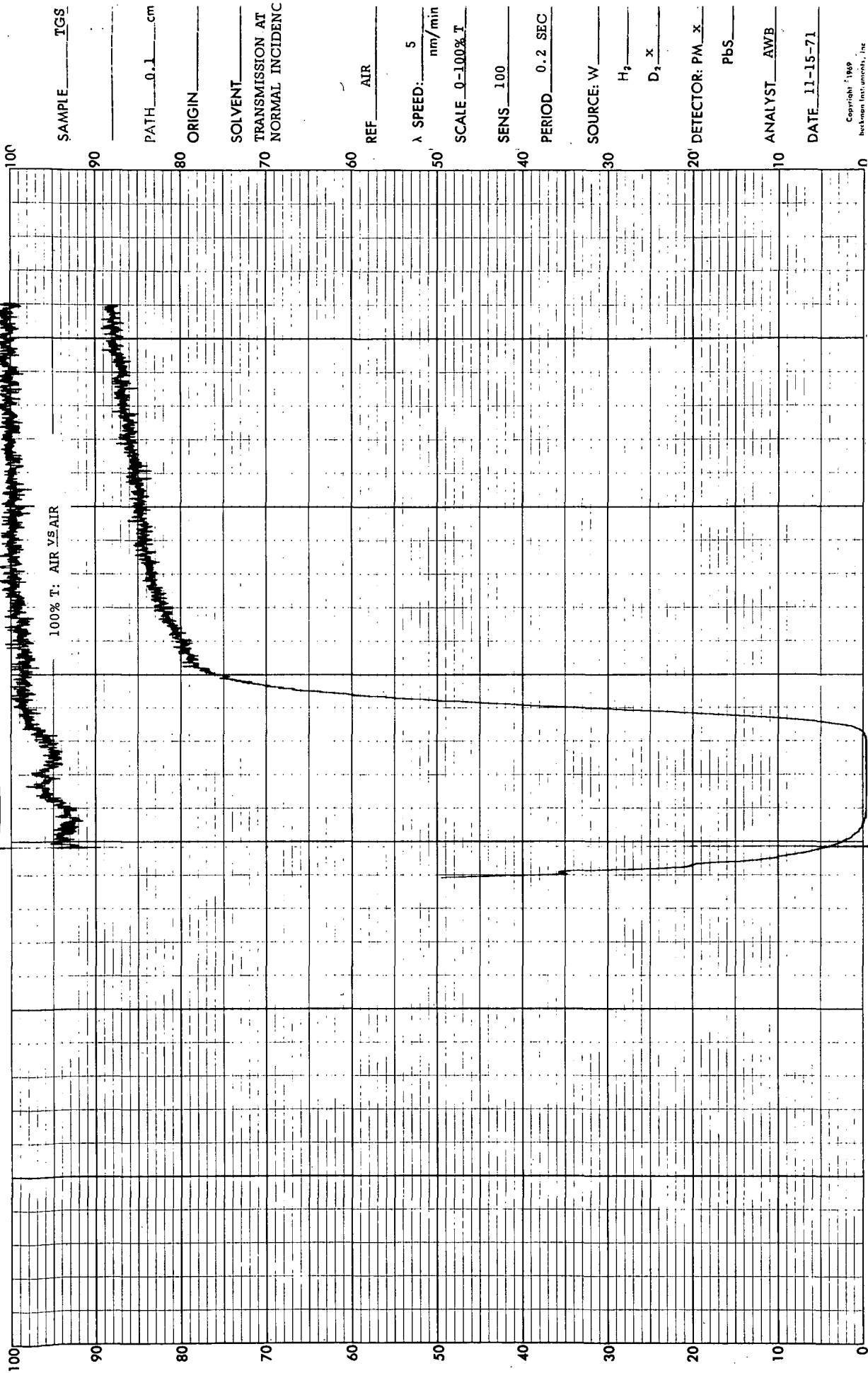
WHEN REORDERING SPECIFY CHART NO. 103441

Beckman

DK-2 CHART

WHEN REORDERING SPECIFY CHART NO. 566402

BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE TGS

PATH 0.1 cm

ORIGIN

SOLVENT

TRANSMISSION AT
NORMAL INCIDENT

REF AIR

λ SPEED: 5
nm/min

SCALE 0-100% T

SENS 100

PERIOD 0.2 SEC

SOURCE: W

H₂

D₂ x

DETECTOR: PM x

PbS

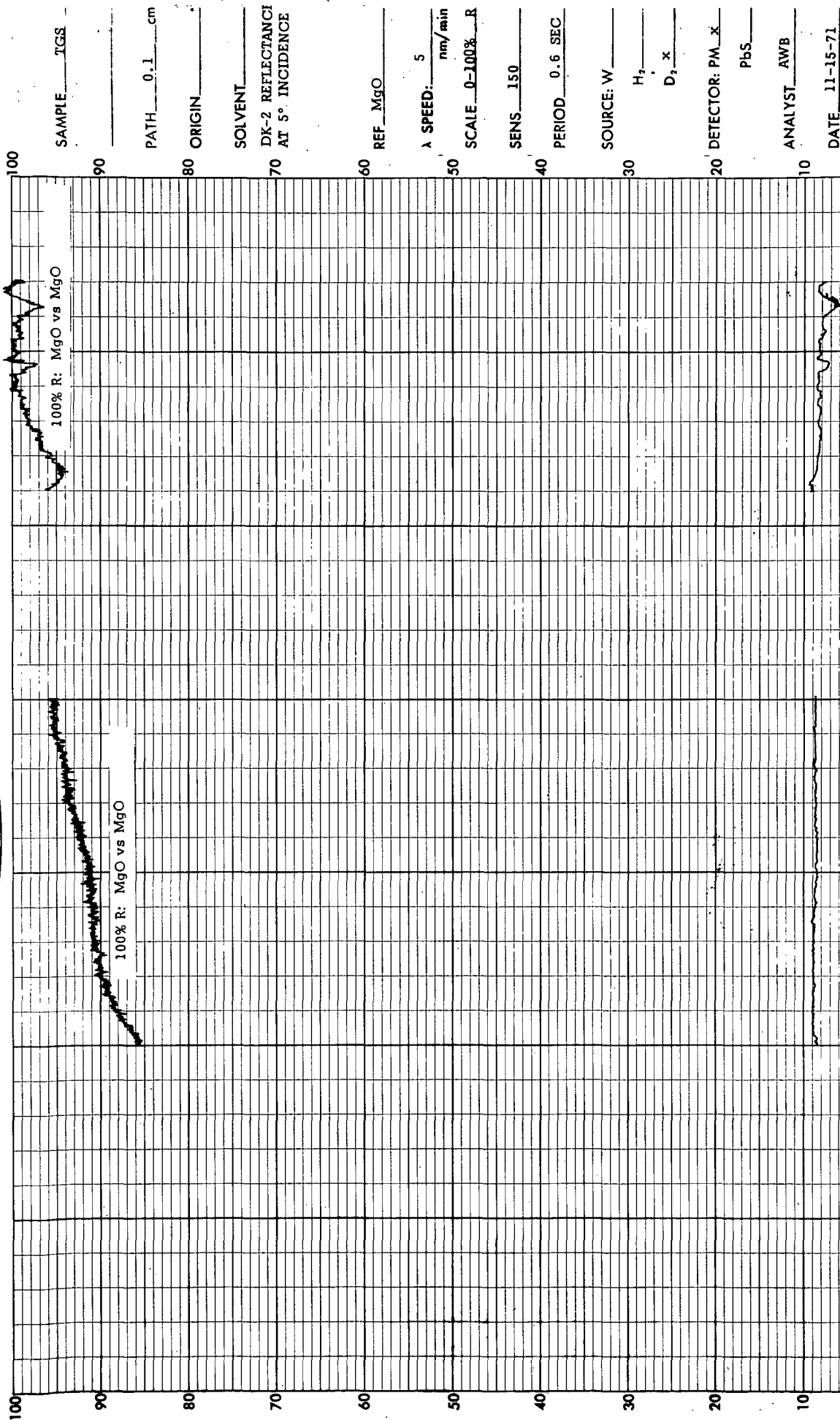
ANALYST AWB

DATE 11-15-71

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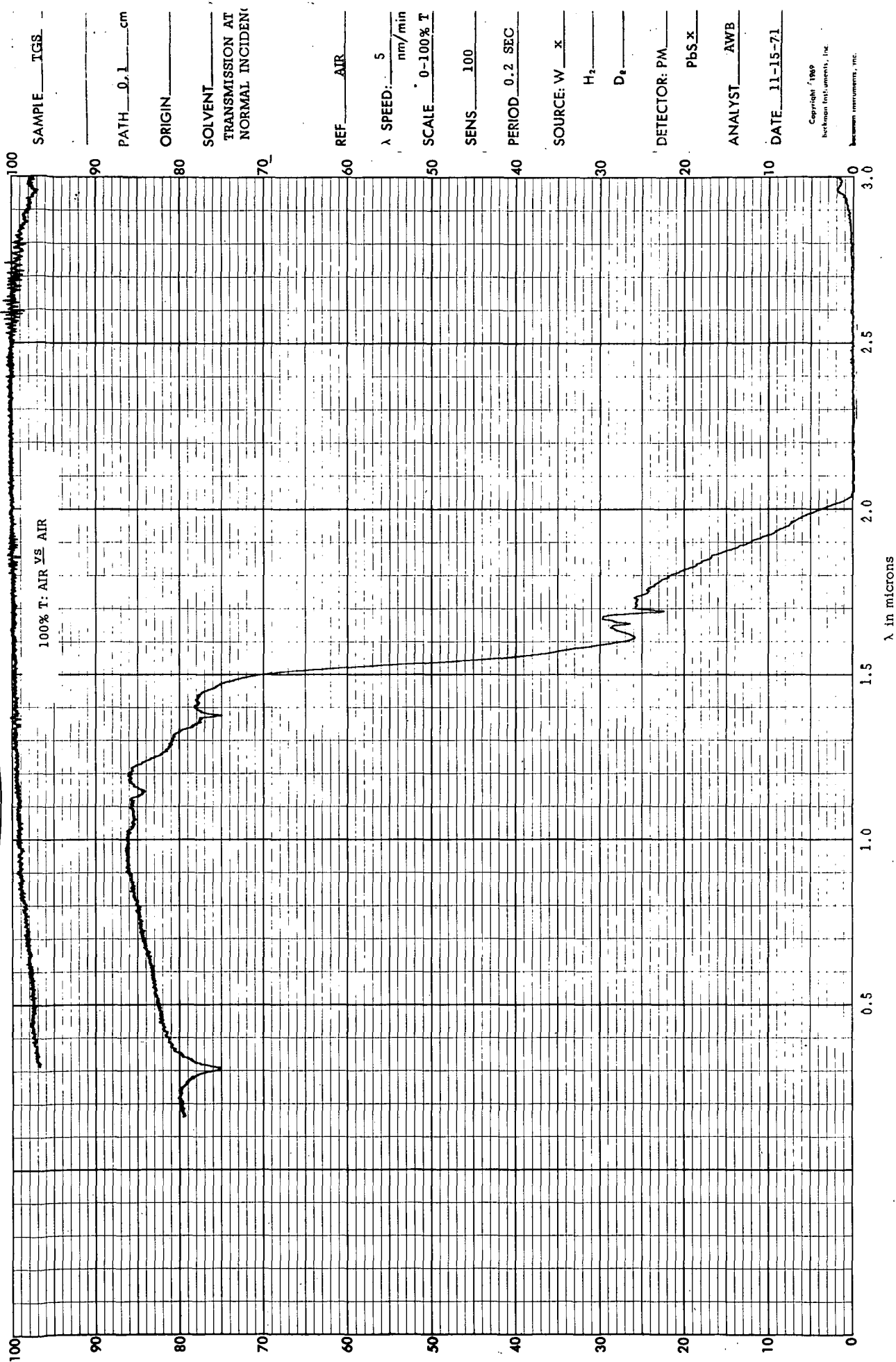
Beckman DK-2 CHART

WHEN REORDERING SPECIFY CHART NO. 566402 BECKMAN INSTRUMENTS INC., FULLERTON, CALIF. U.S.A.



Beckman DK-2 CHART

WHEN REORDERING SPECIFY CHART NO. 566402 BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE TGS
 PATH 0.1 cm
 ORIGIN
 SOLVENT
 TRANSMISSION AT
 NORMAL INCIDENT
 REF AIR
 λ SPEED: 5 nm/min
 SCALE 0-100% T
 SENS 100
 PERIOD 0.2 SEC
 SOURCE: W x
 H₂
 D₂
 DETECTOR: PM
 PBS x
 ANALYST AWB
 DATE 11-15-71

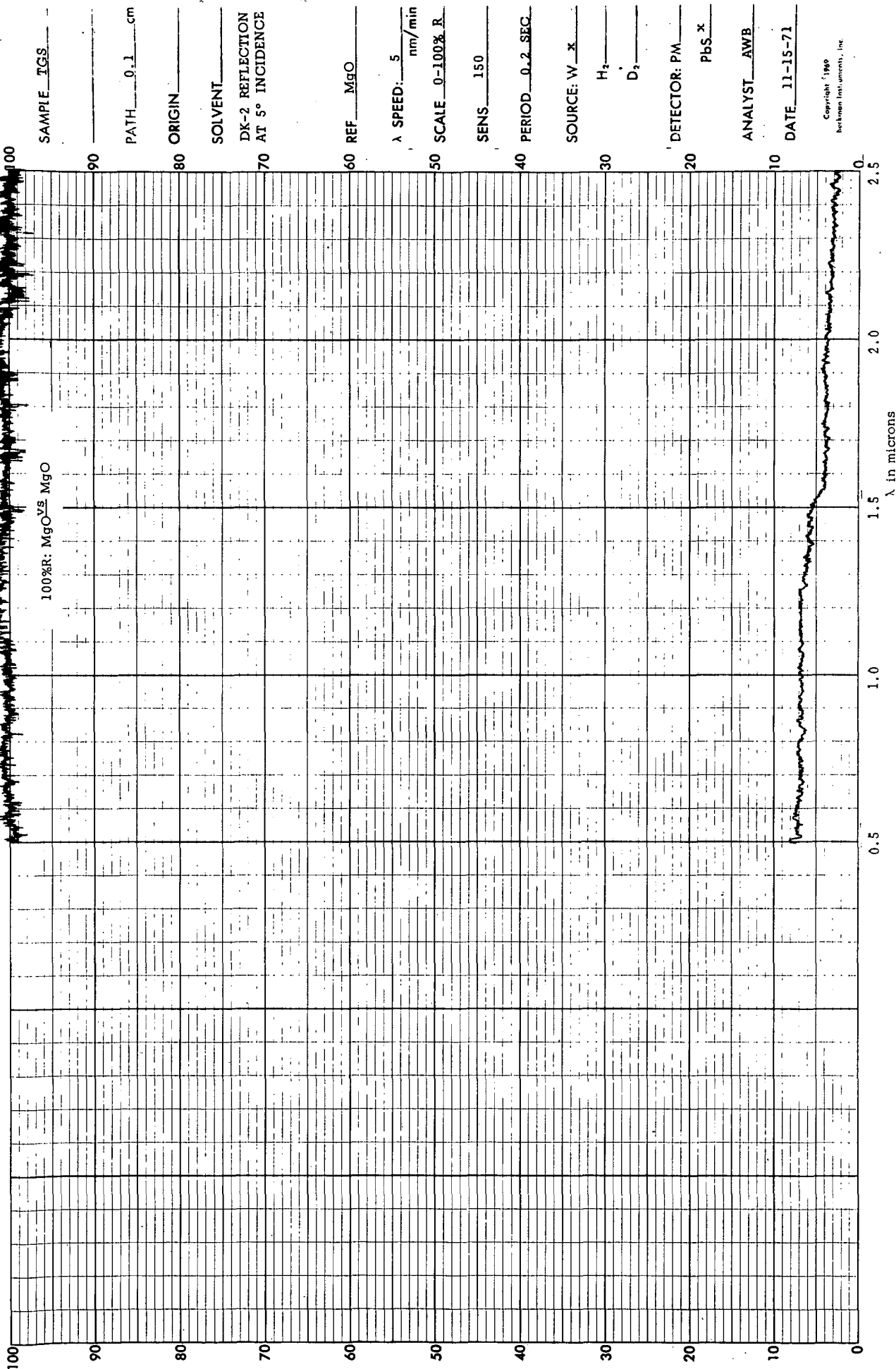
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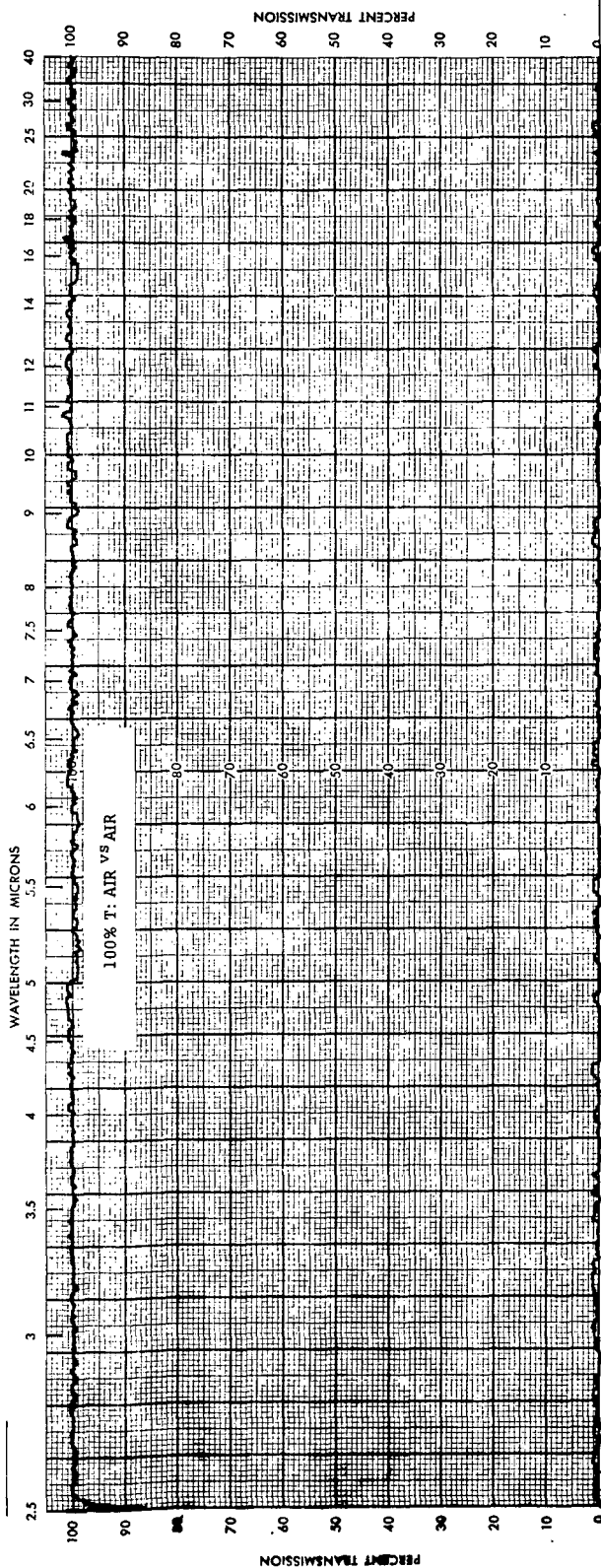
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DK-2 CHART

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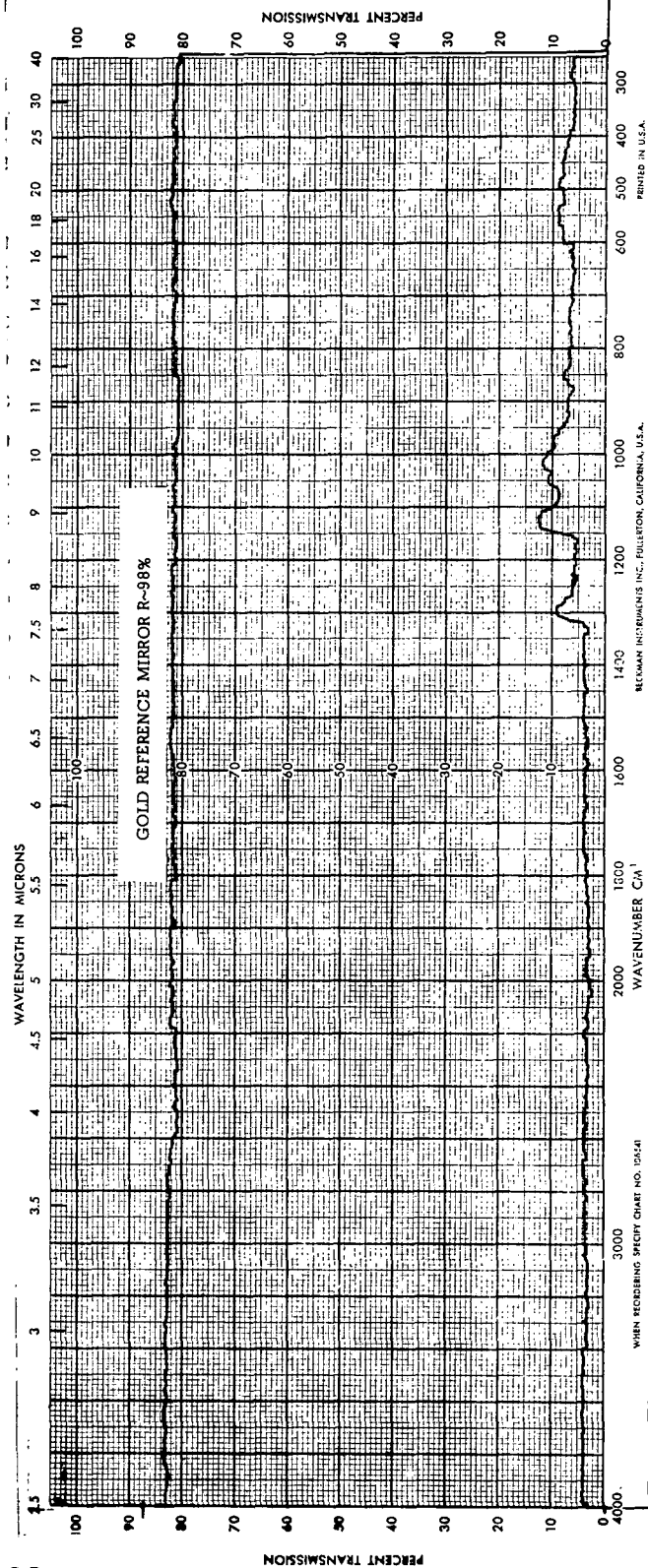
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SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE TGS
 SOURCE BEC
 STRUCTURE _____
 IR-20 TRANSMISSION AT
 NORMAL INCIDENCE
 PATH 1 mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB
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B-20



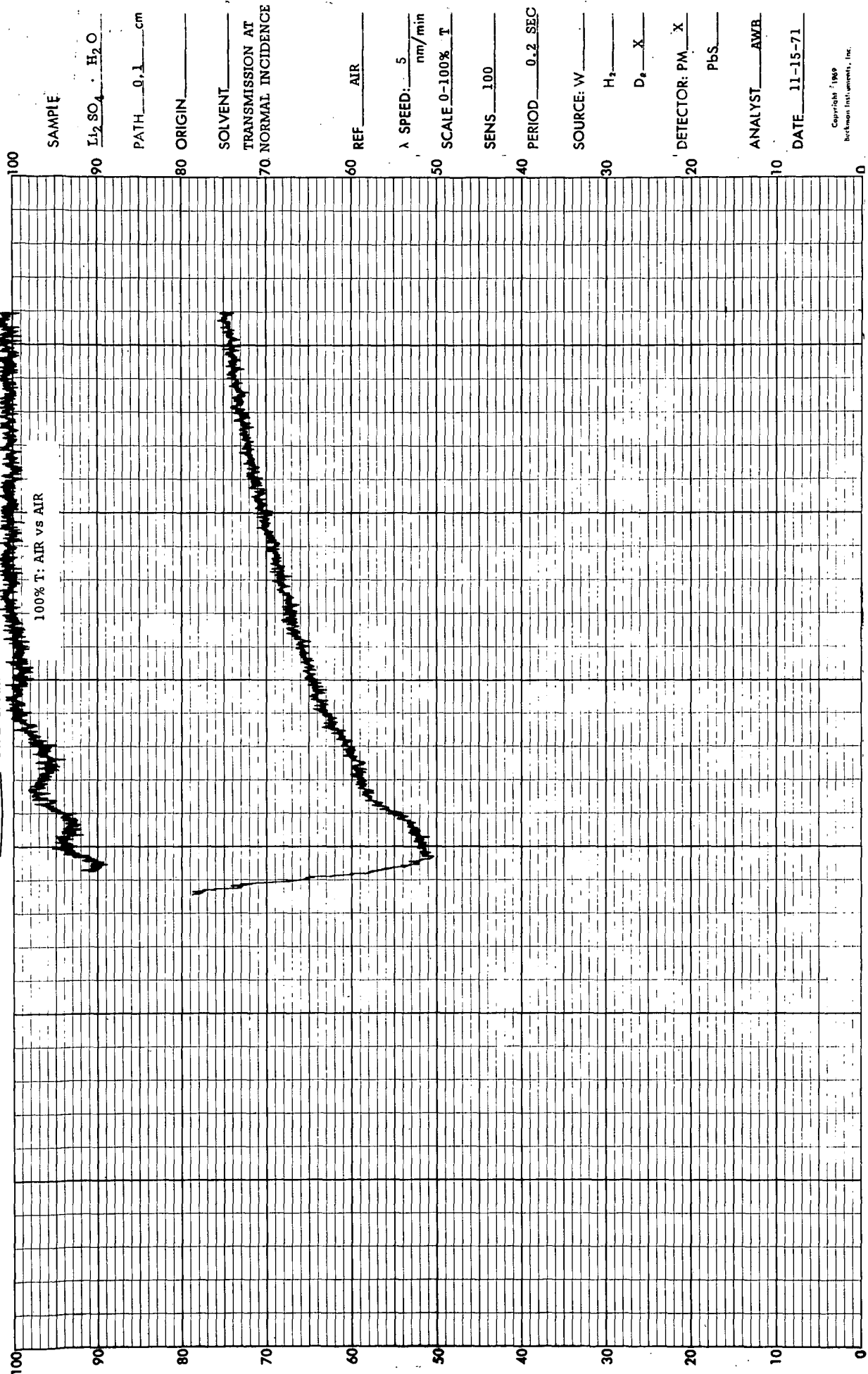
SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE TGS
 SOURCE BEC
 STRUCTURE _____
 IR-20 SPECULAR
 REFLECTANCE AT
 30° INCIDENCE
 PATH 1 mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB
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DK-2 CHART

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SAMPLE

90 $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

PATH 0.1 cm

80 ORIGIN

SOLVENT

TRANSMISSION AT
70 NORMAL INCIDENCE

60 REF AIR

λ SPEED: 5 nm/min

SCALE 0-100% T

SENS 100

PERIOD 0.2 SEC

SOURCE: W

30 H_2

D_2 X

DETECTOR: PM X

PBS

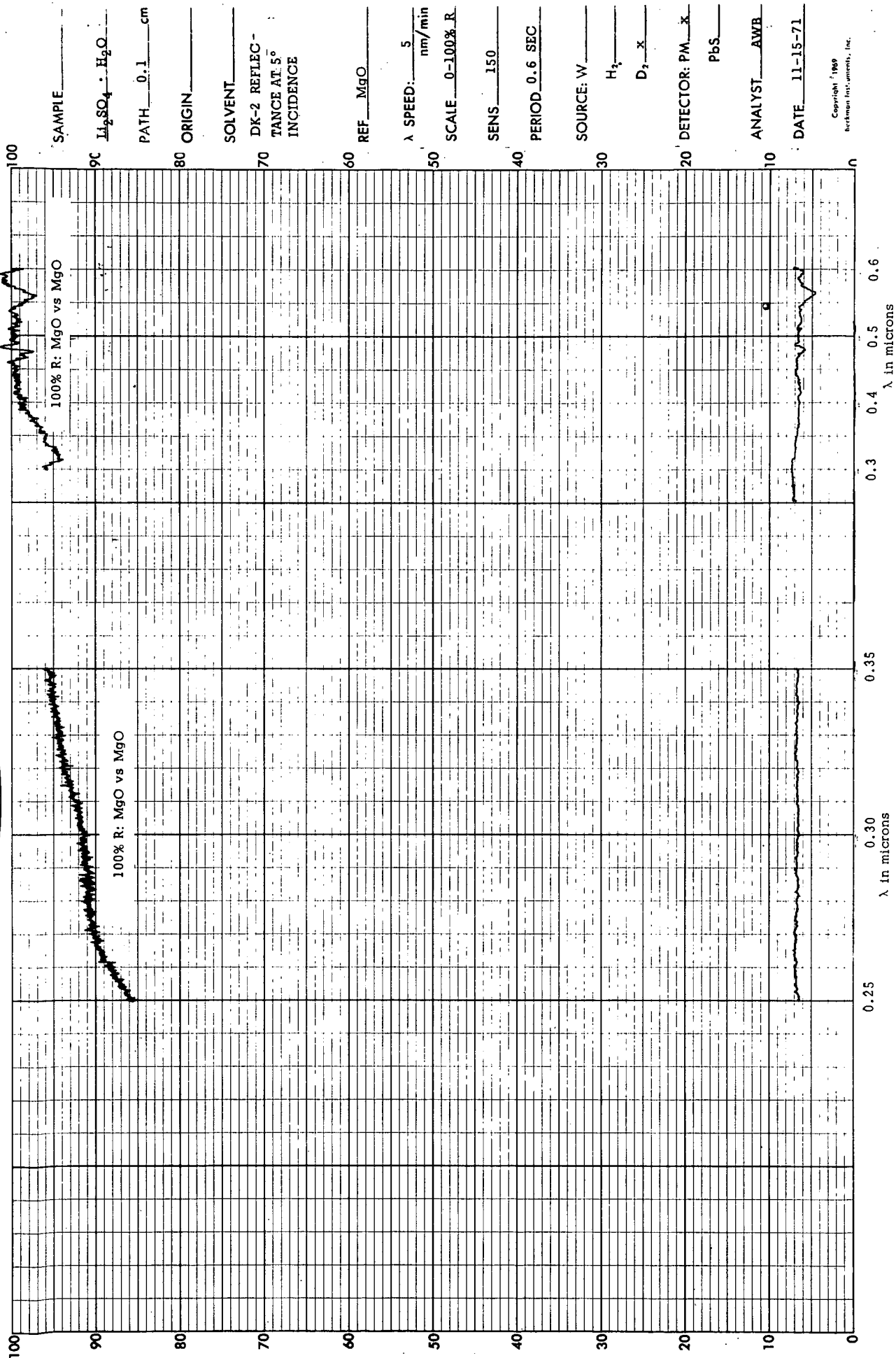
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SAMPLE

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

PATH 0.1 cm

ORIGIN

SOLVENT

DK-2 REFLEC -
TANCE AT 5°
INCIDENCE

REF MgO

λ SPEED: 5
nm/min

SCALE 0-100% R

SENS 150

PERIOD 0.6 SEC

SOURCE: W

H₂

D₂ x

DETECTOR: PM x

PbS

ANALYST AWB

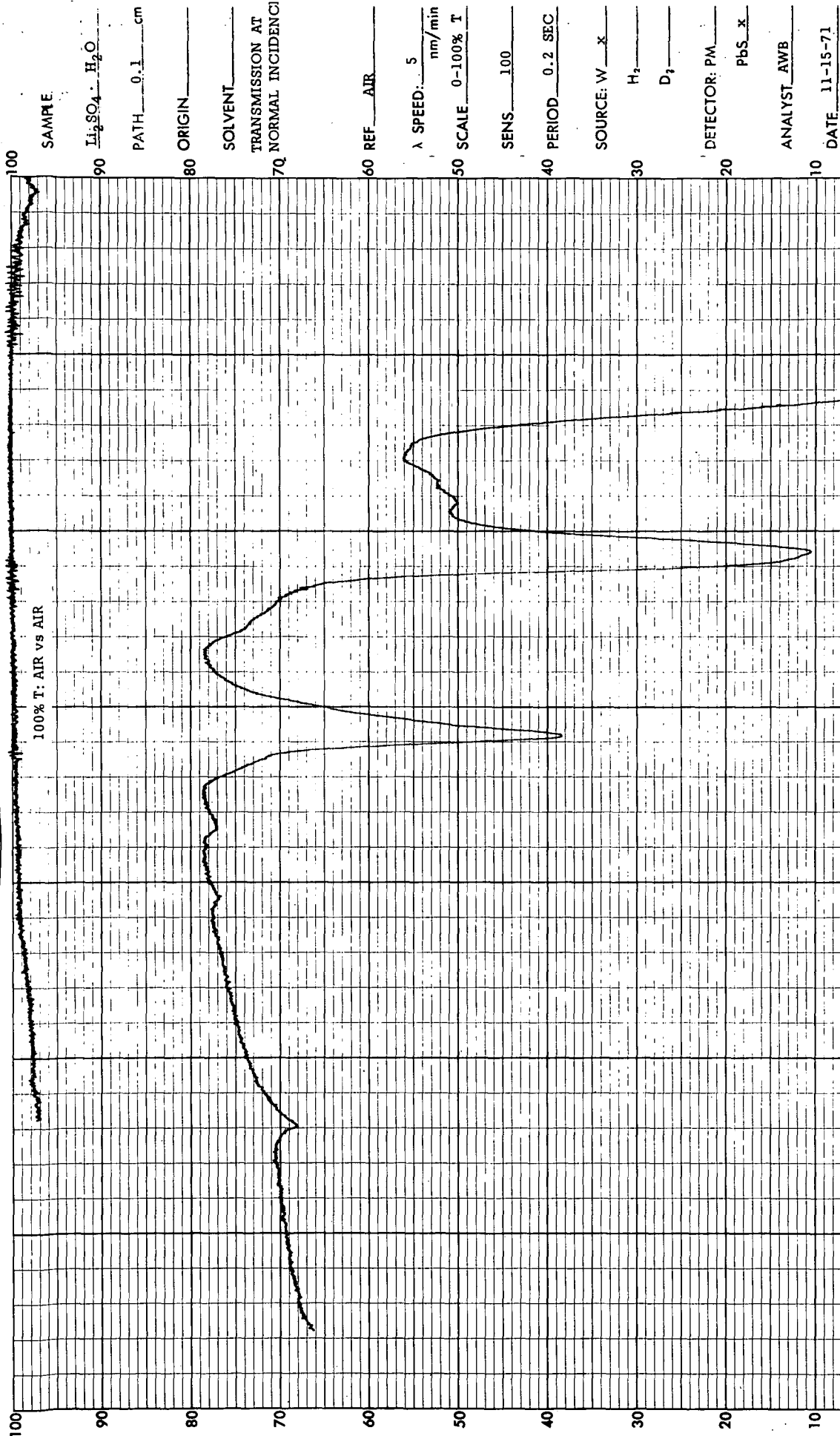
DATE 11-15-71

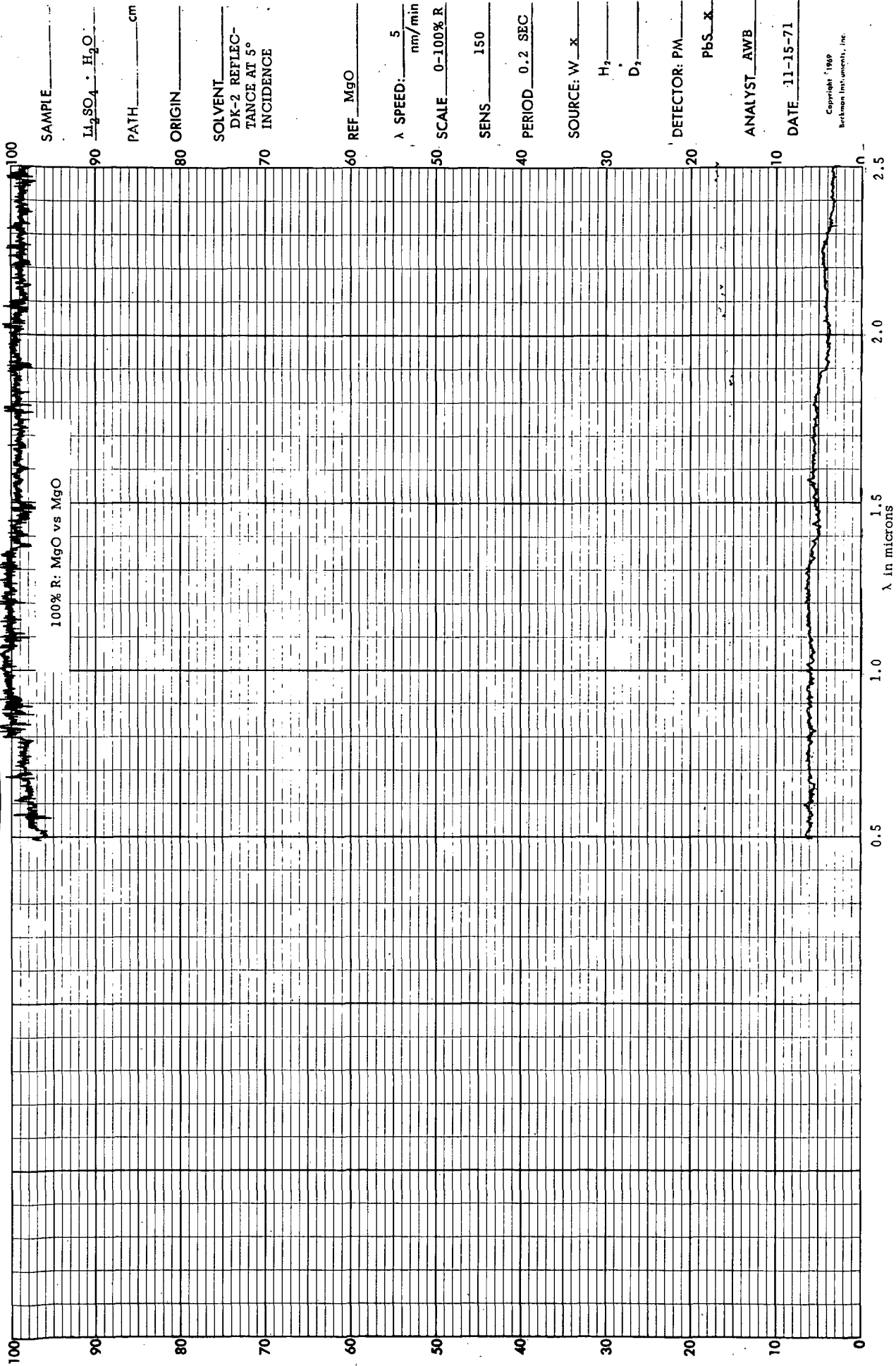
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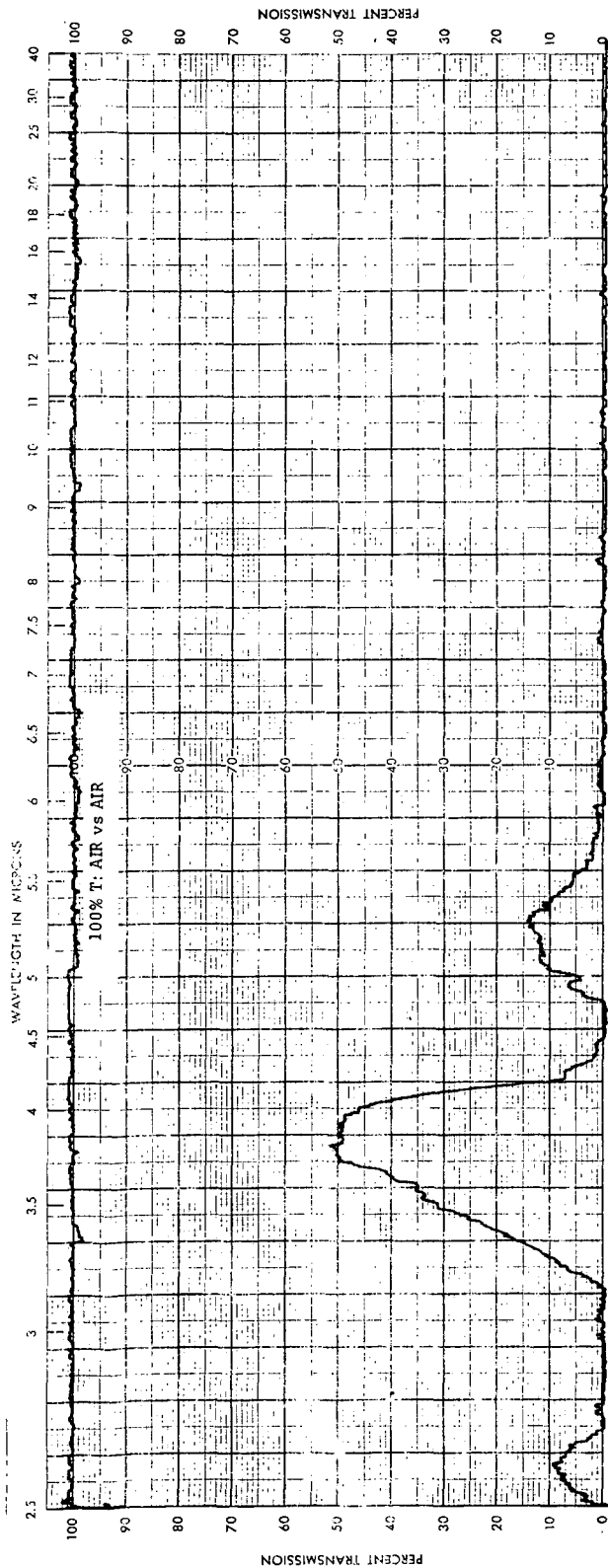
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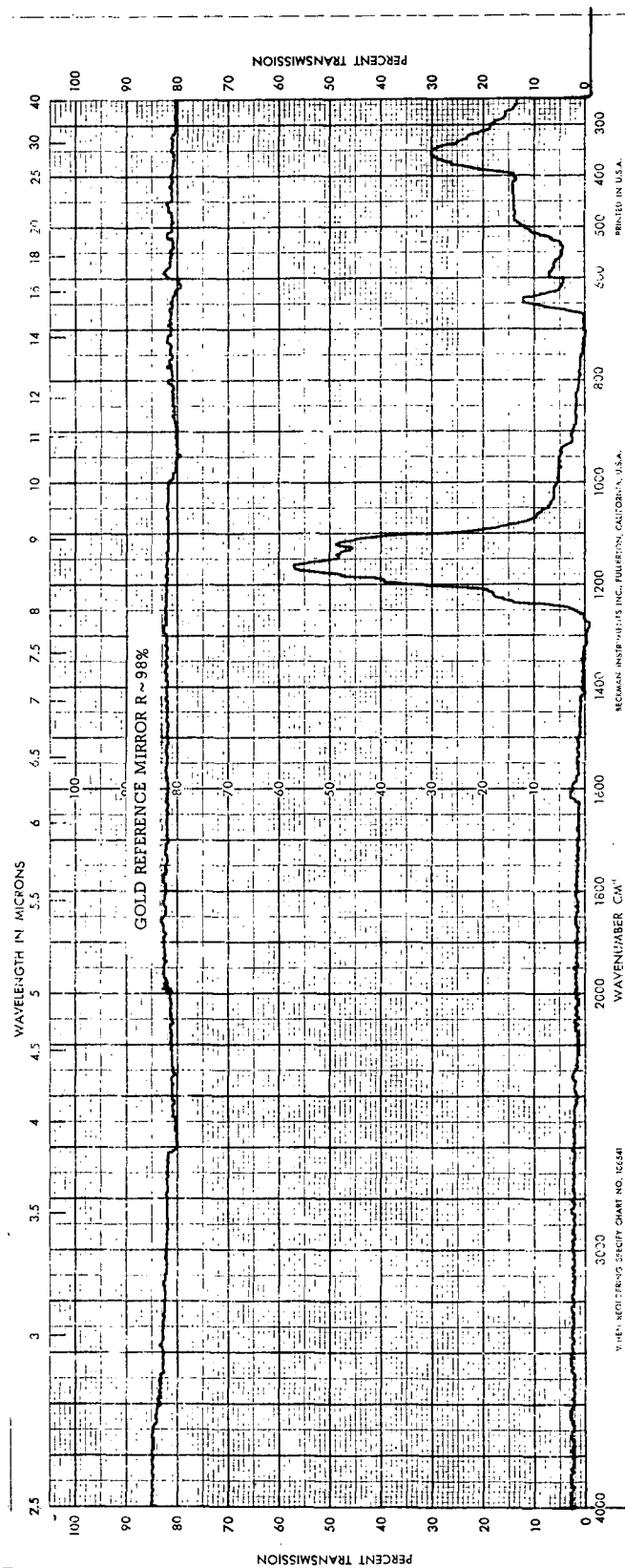




SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
 SOURCE BEC
 STRUCTURE _____
 IR-20 TRANSMISSION AT
 NORMAL INCIDENCE
 PATH 1 mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB
Beckman®



SPECTRUM NO. 11-15-71
 DATE 11-15-71
 SAMPLE $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
 SOURCE BEC
 STRUCTURE _____
 IR-20 SPECULAR REFLEC-
 TANCE AT 30°
 INCIDENCE
 PATH 1 mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB
Beckman®

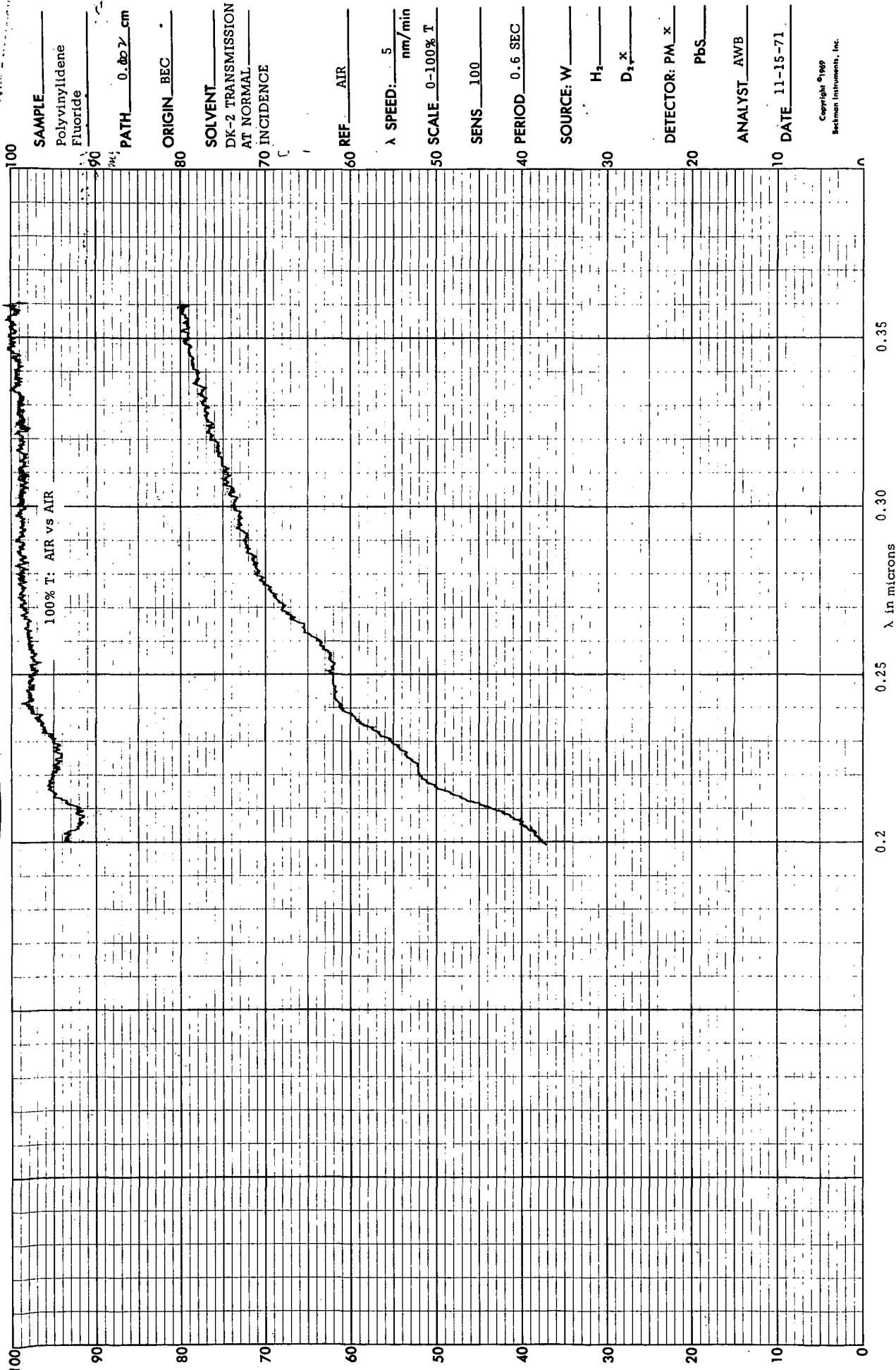


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DK-2 CHART

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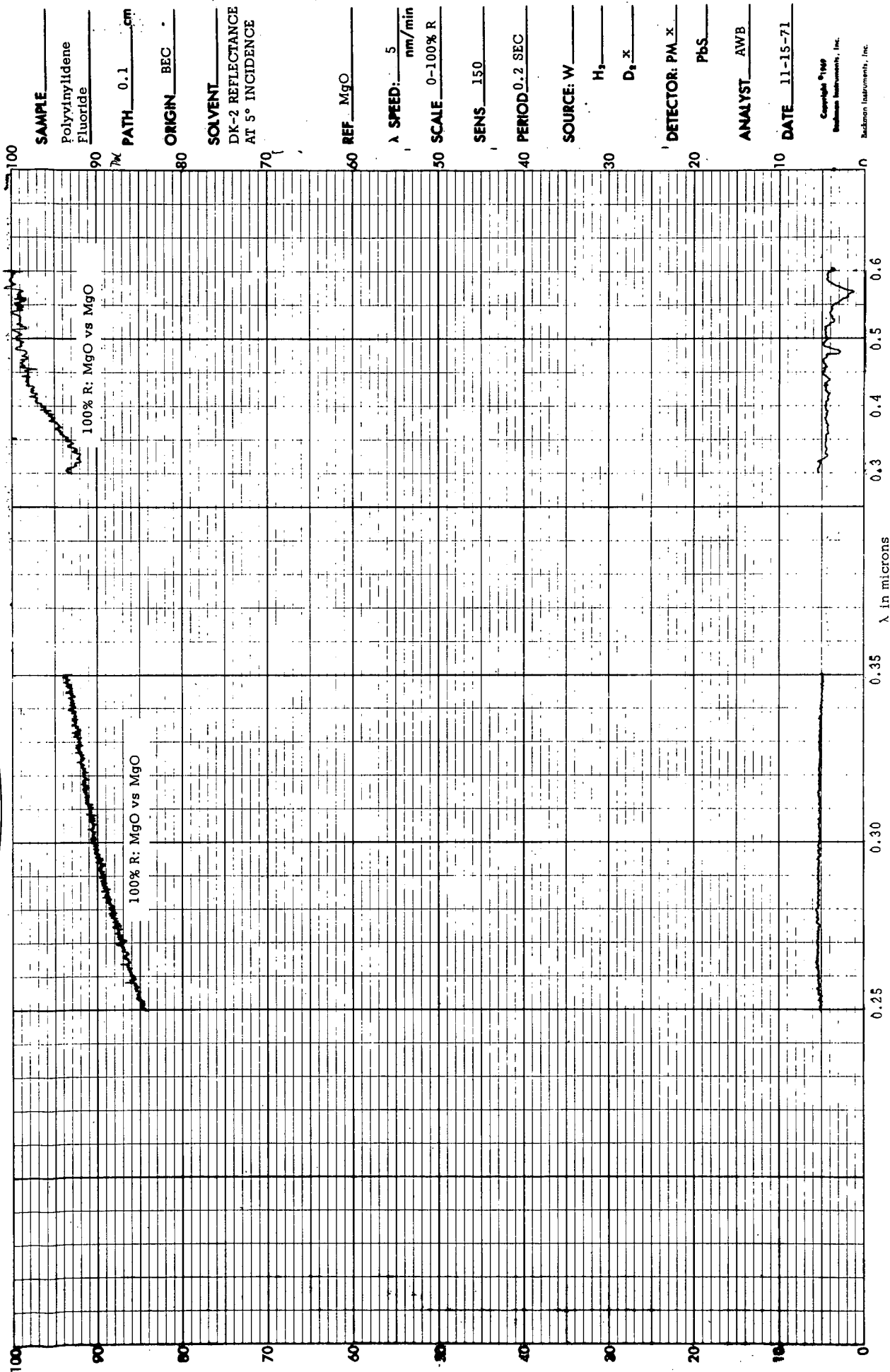
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BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE

Polyvinylidene
Fluoride

PATH 0.1 cm

ORIGIN BEC

SOLVENT

DK-2 REFLECTANCE
AT 5° INCIDENCE

REF MgO

λ SPEED: 5
nm/min

SCALE 0-100% R

SENS 150

PERIOD 0.2 SEC

SOURCE: W

H₂

D₂ x

DETECTOR: PM x

PbS

ANALYST AWB

DATE 11-15-71

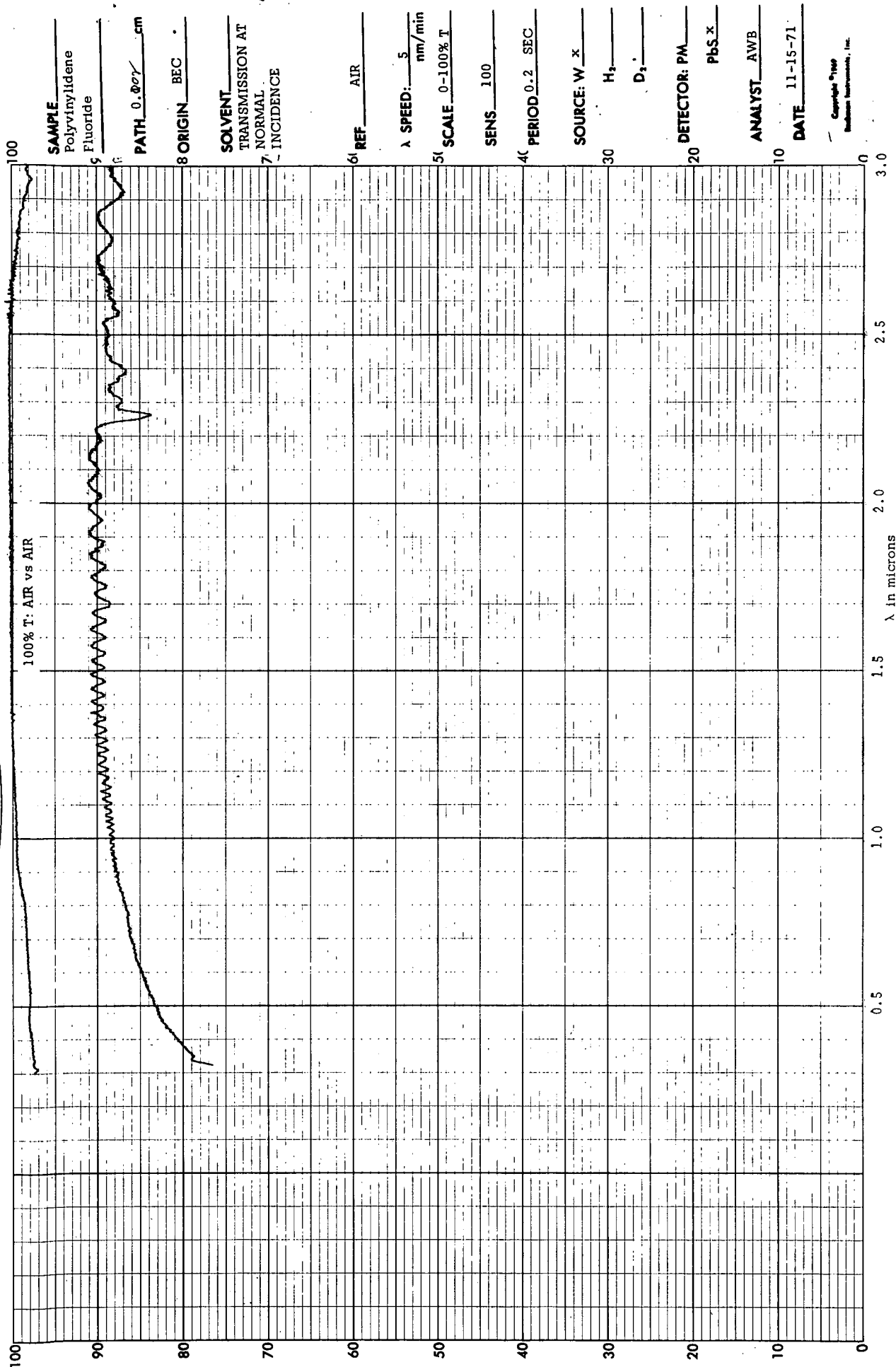
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WHEN REORDERING SPECIFY CHART NO. 566402

BECKMAN INSTRUMENTS INC., FULLERTON, CALIF., U.S.A.



SAMPLE

Polyvinylidene
Fluoride

PATH 0.007 cm

8 ORIGIN BEC

SOLVENT

TRANSMISSION AT
NORMAL
INCIDENCE

61 REF AIR

λ SPEED: 5
nm/min

51 SCALE 0-100% T

SENS 100

40 PERIOD 0.2 SEC

SOURCE: W x

H₂

D₂

DETECTOR: PM

PBS x

ANALYST AWB

DATE 11-15-71

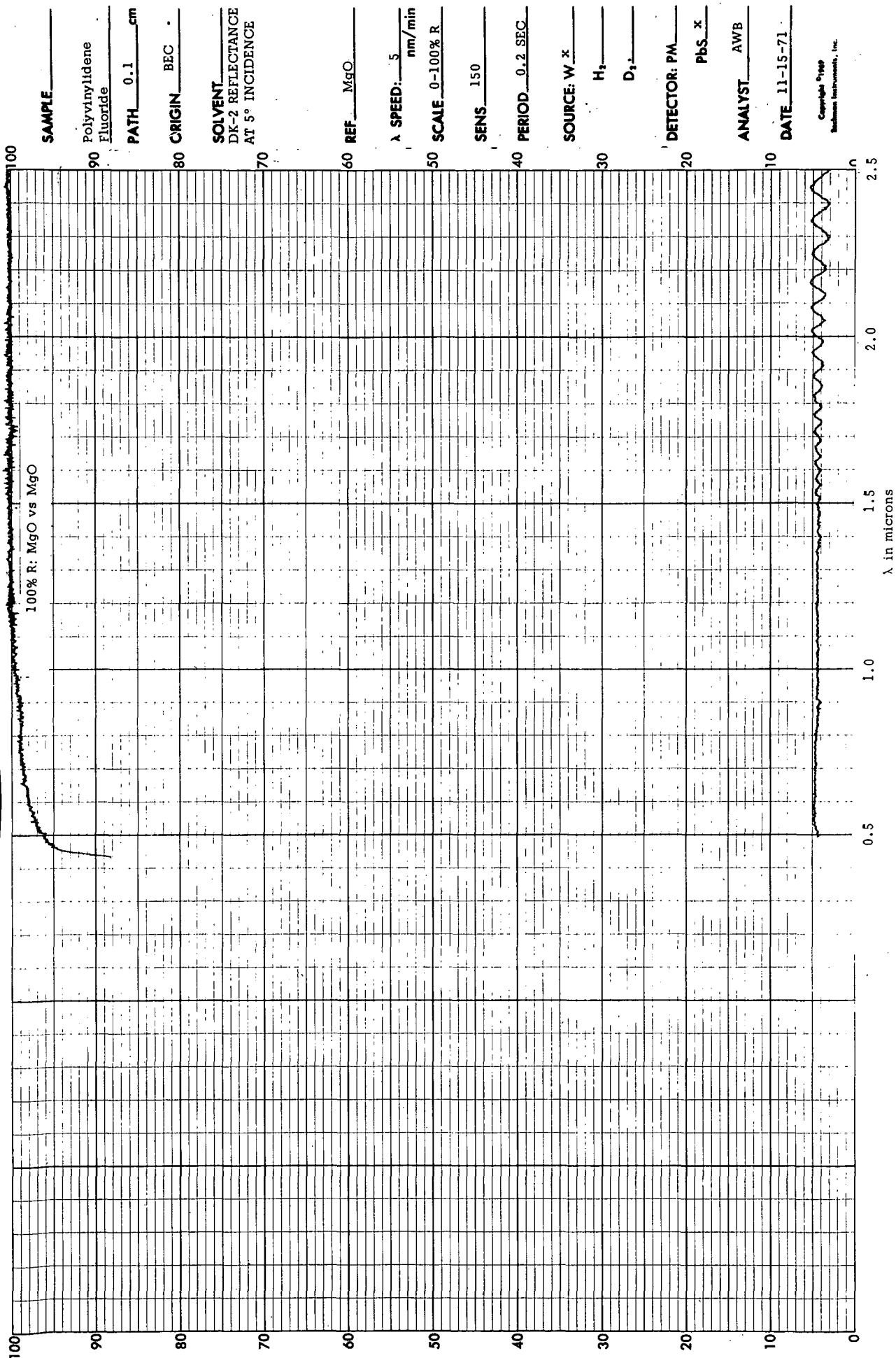
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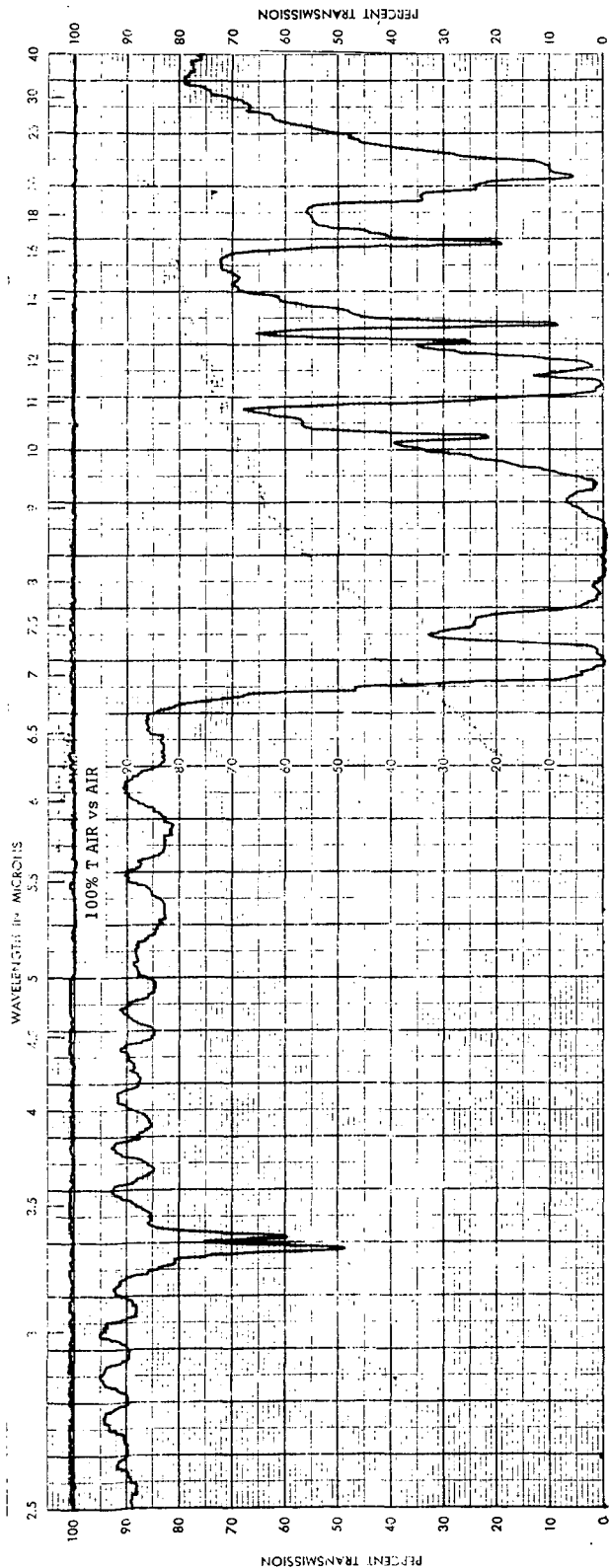
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DK-2 CHART

WHEN REORDERING SPECIFY CHART NO. 566402

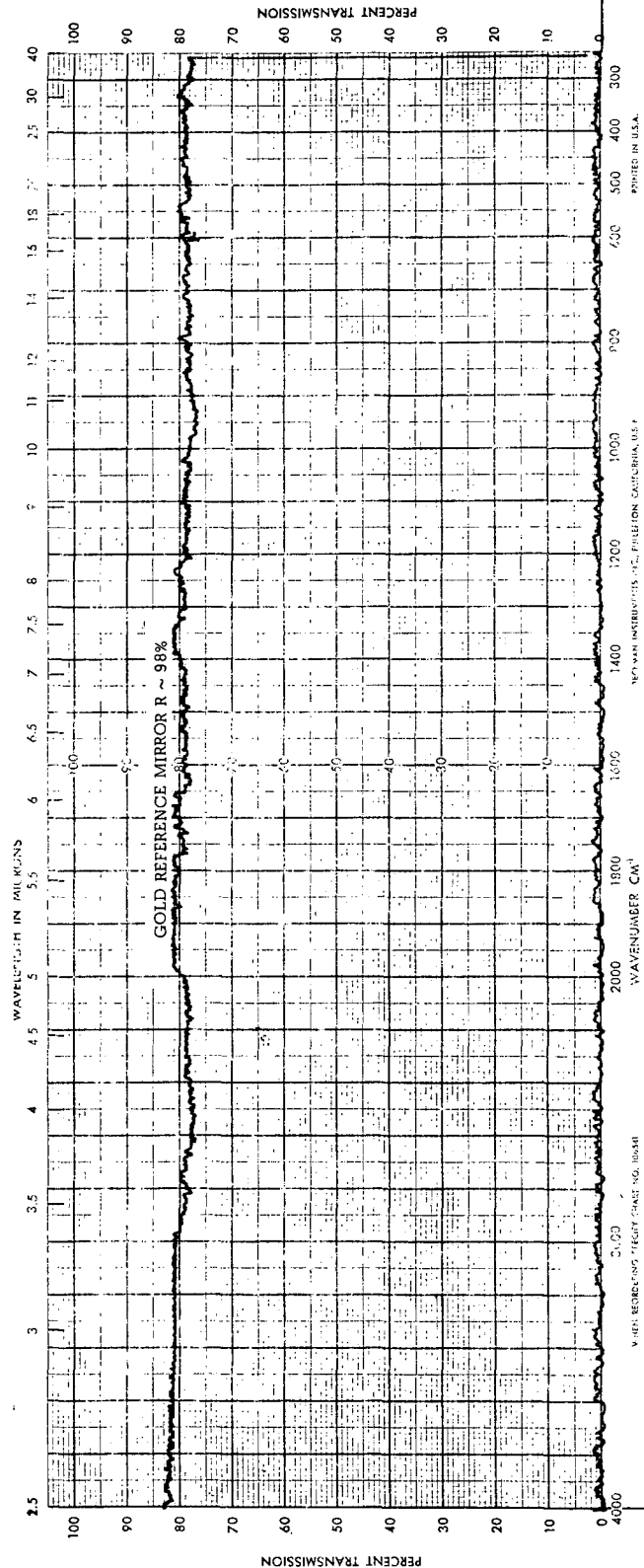
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SPECTRUM NO. _____
 DATE 11-15-71
 SAMPLE Polyvinylidene fluoride
 SOURCE Kofag (Japan)
 STRUCTURE _____
 IR-20 TRANSMISSION AT NORMAL INCIDENCE
 PATH 0.07 mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB
Beckman®

B-30



SPECTRUM NO. 11-15-71
 DATE _____
 SAMPLE Polyvinylidene fluoride
 SOURCE BEC
 STRUCTURE _____
 IR-20 SPECULAR REFLECTANCE AT 30° INCIDENCE
 PATH _____ mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST AWB
Beckman®

SPECTROPHOTOMETER

PERMANENT INSTRUMENTS, INC., FULLERTON, CALIFORNIA, U.S.A.

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